RING-OPENING REACTIONS OF CYCLOPROPYL AND CYCLOBUTYL COMPLEXES OF MANGANESE AND IRON

BY

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To my mother, my husband Gordon
and Dr. S. Gabriel.

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I would like to thank Dr. W.M. Jones for his much appreciated help through the years. He was always there, never laughed too much, and helped me to think more rationally. I will also fondly remember the fellow students in our group, especially Su-Min, Rhonda and Jasson. They certainly made the experience of higher education a pleasure, I think. Finally, I would like to thank Gordon Thorp, my husband, for his support through all the long years. I almost forgot to thank Honda for building good products and allowing about 200,000 miles between 2 cars for my commute from Jacksonville to Gainesville.

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RING-OPENING REACTIONS OF CYCLOPROPYL AND CYCLOBUTYL COMPLEXES OF MANGANESE AND IRON

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August 1989

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Major Department: Chemistry

It has previously been reported that alpha-alkoxy substituted cyclobutyl and cyclopropyl rings, sigma-bound to (dicarbonyl)(n^5-cyclopentadienyl)iron undergo photolytic rearrangement to metallacyclic carbene complexes. This involves a rare alpha-alkyl migration from carbon to metal. It was anticipated that other metal systems would exhibit this alpha-alkyl migration, and with this in mind, the chemistry of alpha-alkoxy sustituted small ring complexes of pentacarbonylmanganese was studied.

Alpha-methoxycyclobutylcarbonyl(pentacarbonyl) manganese was observed to decompose to organic compounds, alpha-methoxycyclobutylcarboxaldehyde and methoxy-cyclobutene in a one-to-one ratio, when thermally, photochemically, or chemically induced with Me_3NO. A trace

amount of methoxycyclobutane was also observed. No evidence for the manganacyclopent-2-ene complex was obtained. Mechanistic studies indicate that a beta-hydride elimination mechanism is responsible for the degradation into organic compounds.

When beta-hydride elimination is precluded due to a high energy barrier, other rearrangements involving alpha-alkyl migration to manganese are observed. For instance, when alpha-ethoxycyclopropylcarbonyl(pentacarbonyl)-manganese is treated with 2.2 equivalents of Me_3NO, formation of (n^3-syn-1-ethoxypropenyl)(tetracarbonyl) manganese occurs. The pi-allyl complex is believed to form from the presumed intermediate: (tetracarbonyl),2-ethoxymanganacyclobut-2-ene by a 1,2 hydride shift.

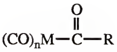
Thermolysis of endo 7-methoxybicyclo(4.1.0)heptyl,7-carbonyl(pentacarbonyl)manganese results in formation of 2 isomeric acyl carbene complexes. It is believed the isomeric nature exists because of the cis or trans positions the 1- and 6-hydrogens can assume. The analogous endo 7-methoxybicyclo(4.1.0)heptyl,7-carbonyl(dicarbonyl)-(n^5-cyclopentadienyl)iron undergoes a photolytic rearrangement to form isomeric acyl carbene complexes. These isomers exist because of the endo- or exo-relationship the 1- and 6-hydrogens can assume with the cyclopentadienyl ligand. X-ray structures for both syn- and anti 1-(carbonyl-n^5-cyclopentadienyl)-2-methoxyferracyclopent-2-ene-5-one,3,4-tetramethylene are reported.

The stereochemistry of the C2-C3 cyclopropane bond-opening of a cyclopropyl Fp alkyl complex has been determined. Photolysis of trans 2-methylcyclopropyl (dicarbonyl)(n^{5}-cyclopentadienyl)iron results in formation of the exo,syn isomer of n^{3}-methallyl(carbonyl)(n^{5}-cyclopentadienyl)iron. Therefore, the C2-C3 bond-opening occurs in a disrotatory manner away from the iron center.

CHAPTER I

INTRODUCTION

The widespread occurrence of transition metal acyl 1 and alkyl 2 complexes has resulted in a tremendous number of mechanistic studies with regard to their rearrangements. These rearrangements typically occur under thermal or photolytic conditions.(1)



$(\mathrm{CO})_n\mathrm{M}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{R}$

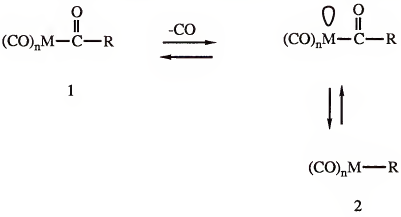
1

$(\mathrm{CO})_n\mathrm{M}-\mathrm{R}$

2

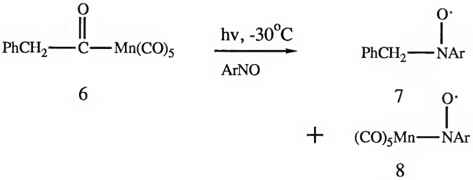
When excess energy is supplied, the result can be either 1) loss of a terminal CO, which provides a site of unsaturation on the metal or, 2) homolysis of the metal-acyl or metal-alkyl bond resulting in organic radicals and metal-centered radicals which undergo further chemistry.

With regard to acyls, loss of CO is the more observed route and leads reversibly to a metal alkyl species.



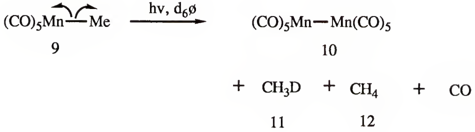
These steps have been extensively studied in the pentacarbonyl manganese system where R=Me under thermal conditions.(2) However, these general steps are not limited to either manganese or metal systems containing strictly carbonyl ligands. Other ligands can be present such as cyclopentadienyl or phosphines.(1)

There are fewer examples of metal-acyl homolytic cleavage, usually occurring when R=$CH_2(Ph)$, $-CH(Ph)_2$, or $-CH_3$. In these cases there are no accessible beta-hydrogens. For example, trapping of radical species in the photolysis of 6 was accomplished by use of an ArNO reagent (Ar=C_6HMe_4) and esr methods.(3)



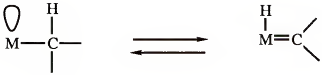
Yet even in this study, it was not directly ascertained whether the source of $PhCH_2$-radical was a result of Mn-acyl bond homolysis, followed by rapid decarbonylation to $PhCH_2$-radical, or metal-alkyl homolysis. The alkyl complex could be easily formed by R group migration in the unsaturated acyl complex.

The general modes of rearrangement available to metal-alkyl complexes beyond terminal CO loss depend largely on the structural features of the R group. Generally, when R does not possess beta-hydrogens, the end result of photolysis or thermolysis is metal-carbon bond cleavage. Photolytic decomposition of $MeMn(CO)_5$ 9 in d_6-benzene produces CH_4, CH_3D, and $Mn_2(CO)_{10}$.(4) The methyl radical is proposed to abstract a hydrogen from another methyl group or a deuterium from solvent.



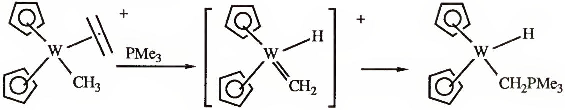
Even though the final products 10 through 12 are formed via free radical reactions, the formation of CO confuses the simple explanation of initial M-C homolysis. Photolytically induced loss of CO from $MeW(CO)_3Cp$ and $MeFe(CO)_2Cp$ systems has been shown to occur at low temperatures.(5) Cleavage of the $M-CH_3$ bond in 9 may occur after initial loss of CO to produce the 15-electron radical, $(CO)_4Mn$.

Another mode of rearrangement is available to unsaturated methyl complexes because of the alpha-protons they possess. Alpha-hydride elimination leads to a hydrido-carbene species, and is becoming more common, especially in metathesis reactions.(6)



14 15

An early example was discovered by M. Green and workers.(7) The tungsten complex 16 thermally loses a pi-bonded ethylene ligand and undergoes an alpha-hydride shift forming a cationic hydrido carbene intermediate 17. This intermediate is trapped by the trimethylphosphine ligand and 18 is isolated.



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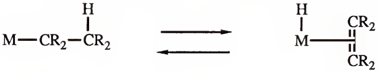
By far, the most common mode of rearrangement for unsaturated metal alkyls is beta-hydride elimination.(1)



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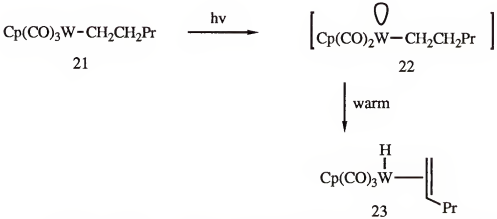
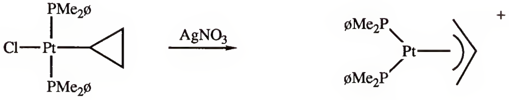
Infrared data has provided direct evidence of a pi-hydride species such as 20.(8) Flash photolysis of 21 at room temperature creates a vacant site by photoejection of

CO, and allows the unsaturated acyl to thermally rearrange[5] to the pi-hydride complex 23. The complex 23 is stable enough at room temperature to allow characterization of its terminal CO vibrations in solution, but it cannot be isolated. At low temperatures around 77 K, Wrighton was even able to spectrally identify the 16 electron intermediate 22.



To summarize to this point, metal alkyls may undergo 1) beta-hydride elimination, 2) alpha-hydride elimination , or 3). metal-carbon bond homolysis. Recently, another type of reaction involving migration of a carbon-containing portion of R onto the unsaturated metal was observed.(9,10) The migration of an alkyl group onto a metal center usually requires a special thermodynamic feature.

The relief of strain is a common mechanistic theme in organic chemistry. A reliable source for the strain energies of cyclopropane and cyclobutane gives values of 28.3 and 27.4 kcal/mol respectively.(11) Thus, upon ring opening, a considerable amount of stabilization is achieved by any compound containing such. This relief is a major driving force for the rearrangement shown below involving the bisphosphine platinum complexes.(9,10)



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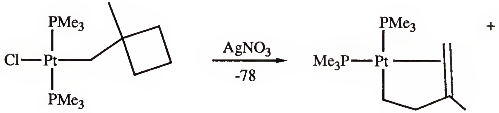

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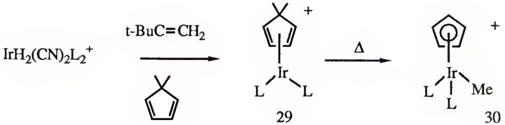
Aromatization is another method of achieving an alkyl migration onto a metal center. Methyl migration from an eta-four bonded cyclopentadienyl ligand resulted in the first example of an alkyl migration from an unstrained alkyl group to a metal center.(12)



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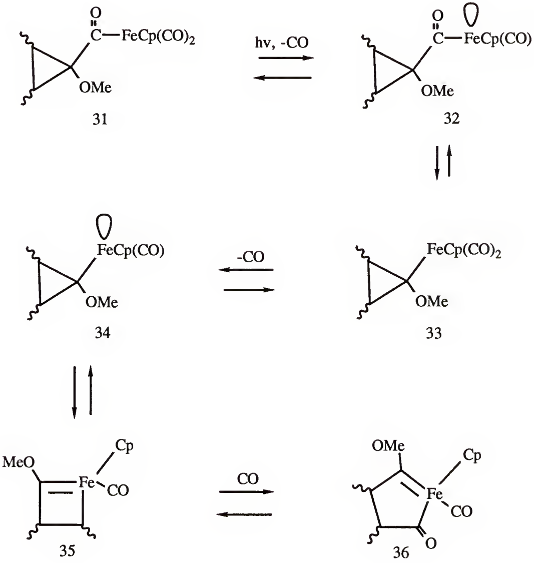
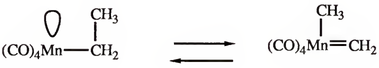
Recently, Jones and Lisko discovered that upon photolysis of the alpha-methoxycyclopropyl iron acyl 31, the metallacyclic carbene 36 was formed.(13)



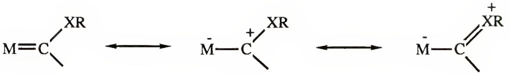
The scheme proposed involves formation of an unsaturated sigma complex 34 which readily expands to the intermediate carbene 35 via an alpha-alkyl migration. The strained metallacyclobutene undergoes carbonyl insertion to the isolable metallacyclopentyl acyl carbene complex 36. The saturated cyclopropyl sigma complex 33 can also be isolated from solution of an incomplete photolysis and transformed into carbene 36 by further photolysis.

Hoffmann and coworkers have theorized as to the energetics involved in this rather experimentally rare alkyl migration to form a metal carbene.(14)



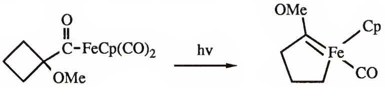
37 38

Using EHMO, they have found the activation barrier for the forward reaction to be only 2 kcal/mol higher in energy than the reverse alkyl migration from the carbene complex 38. (It should be noted that a more recent paper has found a much higher activation energy for the forward reaction.(15)) This provides some insight for the formation of 36, that is, the strain relief of cyclopropane opening must provide an extra push. But just as important is the resonance stabilization of the resulting Fischer-type carbene by the alpha methoxy group. Fischer carbenes are highly polarized in the manner shown below, and most carbenes of this type have heteroatom or phenyl groups to provide the necessary electron density. Carbenes without such groups have been prepared, but only at low temperatures, and are reacted in situ.(16)



39 40 41

Other suitably strained $Cp(CO)_2Fe$-acyls and -alkyls also undergo this rearrangement.(17,18)



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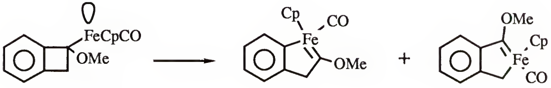
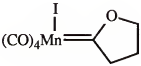


44 45 46

In all cases studied thoroughly, both relief of ring strain and an electron-donating substituent in the alpha position on the organic ring are required for this rearrangement to occur. Also, the only metal system found to undergo this reaction up to date is the $Cp(CO)_2Fe$-system. It was of interest to determine whether any other metal systems could undergo this reaction and form an isolable carbene complex. The metal system chosen for study was the pentacarbonylmanganese moiety. The reasons for its choice begin with the known synthesis of manganese acyls using easily generated $(CO)_5Mn$ anion(19) with the appropriate acid chloride. Manganese acyl complexes generally undergo thermal decarbonylation to the alkyl complex. Furthermore, the theoretical calculations of Hoffmann, as to the feasibility of an alkyl shift to carbene, used the $(CO)_4Mn$ system, perhaps because of the symmetry, but none the less give an estimate of the plausibility of such a reaction. It should be noted that there were no isolable alkyl manganese carbenes prior to the results within this research group. There are, however, examples of tetracarbonylmanganese carbenes that contain a halogen ligand such as in 47.(20) Closely related is the dinuclear carbene 48, synthesized by King but whose structure was determined by Casey.(21,22)



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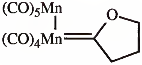

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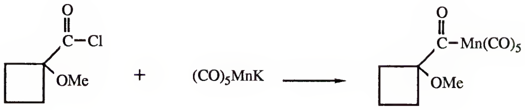
CHAPTER II

ALPHA-METHOXYCYCLOBUTYLCARBONYL (PENTACARBONYL)MANGANESE

The alpha-methoxycyclobutyl acyl of pentacarbonylmanganese was the first small, strained ring complex of manganese to be synthesized. Its chemistry, both thermal and photochemical, was thoroughly studied. Unfortunately, its chemistry was not identical to its (dicarbonyl)(η^5-cyclopentadienyl)iron-counterpart. Much of the research carried out on acyl complex 51 was concerned with its degradation into organic compounds.

Synthesis and Decarbonylation of (51)

The manganese acyl complex 51 was synthesized in typical yields of fifty percent from the reaction of acid chloride 50(17) with pentacarbonyl manganese anion.



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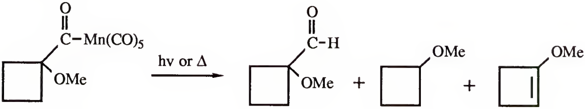
51

The remainder of this chapter will describe the various methods and results of decarbonylation of acyl complex 51, including thermolysis, photolysis, and chemical removal with Me_3NO.

Manganese acyl 51 readily underwent decarbonylation when heated to 55° C in deuterated benzene. Unless stated otherwise, the reaction solvent used in experiments was deuterated benzene. Three organic compounds, all containing an intact cyclobutyl ring, were formed. Analysis by ^{13}C and ^{1}H NMR showed the compounds to be alpha-methoxycyclobutanecarboxaldehyde 57, methoxycyclobutane 58, and 1-methoxycyclobutene 59.



51 57 58 59

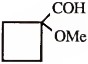
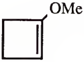
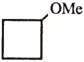
The ratios of these organic compounds formed thermally remained consistent after many repeated experiments. The results are shown in Table 1. These ratios do change slightly when acyl complex 51 is heated at 55° C in d_8-toluene. These same three organic compounds are formed when acyl complex 51 is photolyzed at room temperature in d_6-benzene. Furthermore, the ratios are found to be identical to the ratios obtained in the thermolysis. The overall rate of decarbonylation by photolytic means was slower than by the thermolysis.

Degradation of 51 was also achieved by reaction with Me_3NO in deuterated benzene. The aforementioned organic compounds were again formed and in the same ratios. Identical results from three methods of decarbonylation indicate the same mechanism of decomposition is occurring in each method.

An internal standard, napthalene was used in the thermal decarbonylation of 51. An approximate yield of organic products 57, 58, and 59, based on 51 was obtained. The yield for the sum of these products was 94%. This indicates the acyl complex 51 is not forming a significant amount of any nondetectable product(s). The manganese-containing product of the thermolysis was the dimer $Mn_2(CO)_{10}$. The yield of dimer was not quantified since it was identified by TLC and IR.

The reaction of acyl 51 with Me_3NO was essentially instantaneous and quite vigorous. The manganese-containing product formed was not identified, but it was not the dimer. Many insoluble orange solids were formed and the manganese was most likely a component of these solids. What is enlightening about the reaction with Me_3NO is the mechanism for decomposition of 51 it implies. In all cases studied, Me_3NO reacts with the metal carbonyl complex to remove terminal CO's. It reacts as a chemical decarbonylation reagent.(23) It is believed that attack from amine oxygen occurs at a terminal CO to produce a zwitterion. The zwitterionic intermediate decomposes into unsaturated metal complex, CO_2, and Me_3N. The vacant site

Table 1. Relative amounts of organic products from the various methods of degradation of acyl complex 51.

Reaction conditions			
54° C, d_6-benzene time=48 hours	1.02 (.02)[1]	1.0	0.11 (.01)
25° C, hv, d_6-benzene time=48 hrs	1.06 (.03)	1.0	0.11 (.02)
25° C, 2.2 equiv of Me_3NO in d_6-benzene	1.08 (.03)	1.0	0.15 (.04)
25° C, 1 equiv of $Cp(CO)_3WH$ in d_6-benzene, hv, time=12 hrs	2.03 (.10)	1.0	0.03 (.02)
52° C, d_8-toluene time=48 hrs	1.05 (.01)	1.0	0.06 (.01)
52° C, 5 equiv of 1,4-cyclohexadiene, d_6-benzene	1.04 (.01)	1.0	0.05 (.01)
52° C, 20 equiv of 1,4-cyclohexadiene, d_6-benzene	1.05 (.01)	1.0	0.04 (.02)

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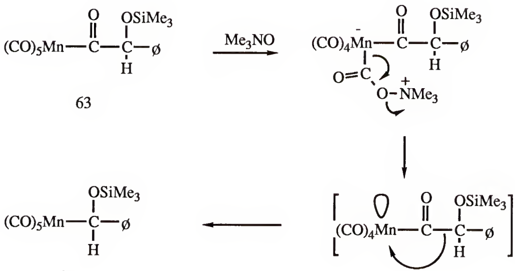
[1] The values in brackets indicate error, in plus or minus value.

on the metal now allows for further reaction. In the example shown, alkyl migration occurs to form a rather rare species, a manganese alkyl complex. It should be noted that alkyl complex 65 is only detected in situ and rapidly decomposes. Trimethylamine oxide has also been used to synthesize phosphine-substituted manganese acyls in less time and higher yields than conventional methods.(24) Usually, the acyl and phosphine are heated together in solution and require long reaction times for phosphine-substitution to occur.


(CO)5Mn—C(=O)—C(OSiMe3)(H)—ø
63
Me3NO
(CO)4Mn—C(=O)—C(OSiMe3)(H)—ø
O=C
O-NMe3
(CO)4Mn—C(=O)—C(OSiMe3)(H)—ø
(CO)5Mn—C(OSiMe3)(H)—ø

65

It is significant that when one equivalent of Me_3NO was reacted with 51, an incomplete decomposition occurred; unreacted 51 remained. It was necessary to use a slight excess of two equivalents for complete decomposition. This is evidence that more than one vacant site is required for formation of the three organic products.

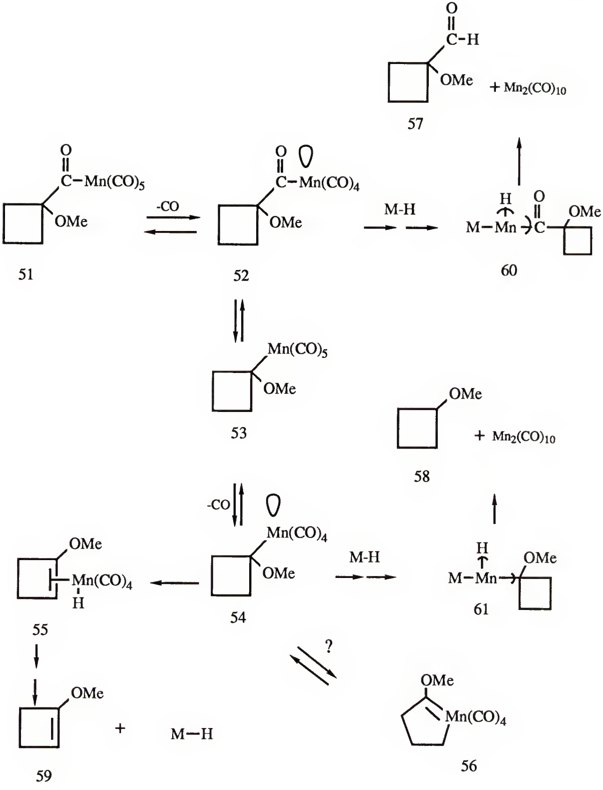
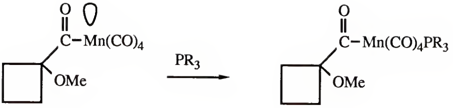


Figure 1. Non-radical mechanism of the degradation of 51.

A rather involved mechanistic scheme is proposed for the degradation of 51, this is shown in Figure 1. Evidence for this scheme is based on the experiments within this chapter. All of the steps in the scheme are well known and have been documented by many researchers.(1,2,5,8) No new mechanism is proposed, but the research into the mechanism of degradation was well warranted since the role of the manganese moiety had to be established. If the degradation occurred by a free radical mechanism, the $(CO)_5Mn$ system would have been abandoned. Fortunately, experimental evidence supports the formation of the unsaturated alkyl complex 54, which is the immediate precursor to the carbene complex 56. Delineation of this mechanism led to the design of other manganese systems which rearranged to carbene complexes.

In this scheme, the first step is loss of one terminal CO from 51 to form the unsaturated acyl complex 52. This occurs as a result of thermolysis, photolysis, or chemical decarbonylation with Me_3NO. Convincing evidence for the intermediate was given by the reaction of 51 with phosphines. Heating or photolyzing 51 with one equivalent of PEt_3 or $P(Ph)_3$ gave the phosphine-substituted acyl 70 as the major product. With the less crowded PEt_3, the triethylphosphine-substituted acyl is the sole reaction product. But with the larger $P(Ph)_3$, other products were formed. These were not new products, but the three organic compounds 57, 58, and 59 that were formed in the absence of phosphines.



52 70

This is consistent with formation of unsaturated 52, since it could be trapped with the PEt$_3$ ligand before undergoing further rearrangement. In the reaction with P(Ph)$_3$, however, the larger size of this phosphine diminished its coordinating ability and alkyl migration to form the saturated alkyl complex 53 sometimes occurred.

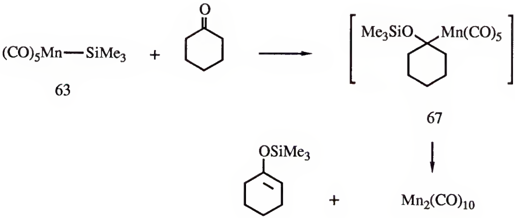
The trapping ability of P(Ph)$_3$ was observed to be temperature dependent. At lower temperatures i.e., 35° C, the reaction proceeded slowly with more phosphine acyl complex forming and lesser amounts of the organic compounds. Higher temperatures resulted in a faster reaction with a greater yield of the organic compounds.

Reacting more than one equivalent of P(Ph)$_3$ also resulted in the formation of more of the phosphine-substituted acyl complex. Both the temperature and the concentration effects on the product ratios are consistent with formation of the unsaturated acyl 52. More thermal energy should favor alkyl migration, thus more organic compounds are ultimately formed.

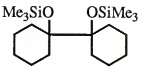
Larger concentrations of P(Ph)$_3$ result in faster trapping of complex 52 and lessen the likelyhood of alkyl migration.

Once the intermediate 52 is formed, it can react by one of two different routes. One route is the previously discussed alkyl migration which forms 53. The second route is oxidative addition of a manganese-hydride species to form the dinuclear species 60.

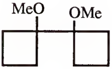
The alkyl complex 53 is never detected by monitoring the photolysis or thermolysis of 51, but its existence is implied by the formation of the cyclobutene 59 and the cyclobutane 58. A quite similar system of Gladysz' in which an alpha-siloxy manganese sigma complex was postulated, but not detected is shown below.(25) The intermediate alkyl complex 67 was found to decompose at room temperature to the cyclohexyl silyl enol ether. This occurs most likely by a beta-hydride elimination mechanism, even though a mechanism was not discussed. It is unlikely a free-radical mechanism is operating here since no organic dimer compound 68 is formed.



The similarities between the products formed in Gladysz' system and those of the title compound are suggestive of a non-radical decomposition. In both degradations the existence of a non-detectable alkyl complex, bearing an alkoxy/siloxy substituent, is postulated. In both situations a cycloalkene is formed, but no organic dimer 68 or 72. The latter two compounds would be formed as a result of a free-radical reaction.

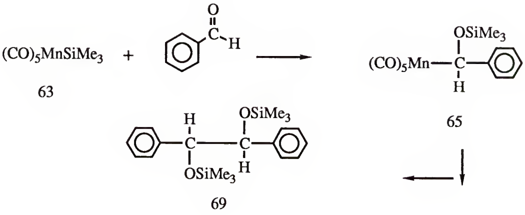


68



72

In contrast, the reaction of 63 with benzaldehyde produces the detectable alkyl complex 65. Alkyl complex 65 has no beta-hydrogens. This condition renders 65 more kinetically stable than 67, which does possess beta-hydrogens. However, 65 has only a limited existence and decomposes by Mn-C homolysis, forming radicals which dimerize. The only organic product detected is 69.

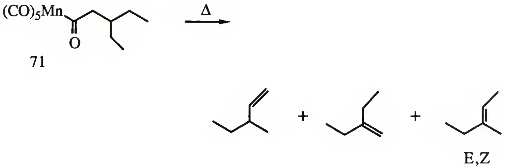


The sigma complex 53, from Figure 1, should also be kinetically unstable and is postulated to undergo loss of a terminal CO to form the unsaturated alkyl intermediate 54. This intermediate could readily form the pi-hydride species 55 through beta-hydride elimination. A small amount of 54 is proposed to react with a manganese-hydride species to ultimately form methoxycyclobutane. This intermolecular reaction is expected to be slower than the intramolecular, beta-hydride elimination.

The pi-bonded alpha-methoxycyclobutene ligand could at this point dissociate, and generate tetracarbonyl manganesehydride. This, or a similar manganese hydride complex, reacts further to eventually form the other two organic compounds, the aldehyde and the alkane. This will be discussed later.

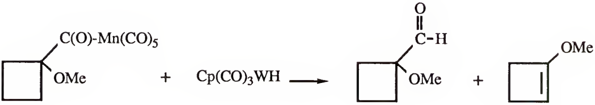
The strain energy of cyclobutane is 27.4 kcal/mol, while that of cyclobutene is 30.6 kcal/mol.(11) The small energy difference between the two should easily allow for formation of alpha-methoxycyclobutene from an appropriate alpha-methoxycyclobutane precursor. With the known, facile beta-hydride elimination process available to metal alkyl complexes, it is most certain that alpha-methoxycyclobutene is formed as a consequence of this process.

Other manganese acyl complexes have been shown to thermally decompose to alkenes. For example, Casey found that thermolysis of 71 gave 4 isomeric hexenes and proposed a series of beta-hydride eliminations from the unsaturated alkyl complex, then reversal of this step to form new metal alkyls.(26) The existence of pi-hydride intermediates are proposed. Eventually, the alkyl complex decomposes since the pi-bonded alkene dissociates from the metal-hydride intermediate. Only a small amount of an alkyl complex could be isolated.



It should be noted that the unsaturated alkyl complex 54 is the immediate precursor to the carbene complex 56, as shown in Figure 1. However, the desired carbene complex 56 was never detected in any of the reactions. This does not exclude the possibility of an equilibrium between the unsaturated sigma complex and 56. This situation has been shown to occur in the analogous iron species.(27) A build-up of carbene complex 56 would not occur because of the draining-away of the cyclobutyl ligand in the form of alpha-methoxycyclobutene. No carbene trapping experiments were conducted.

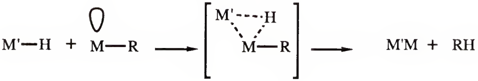
The organic products, aldehyde 57 and cyclobutane 58, are pictured in this scheme as being formed from reaction of a metal hydride with the unsaturated acyl or alkyl complex. The most likely candidate for the metal hydride species is $(CO)_5MnH$, which is most easily formed by CO substitution of the pi-bonded 1-methoxy cyclobutene ligand. That a metal hydride complex may be the source of hydrogen is supported by the ratio of aldehyde to cyclobutene in the reaction of equal equivalents of the tungsten hydride 76 and manganese acyl complex 51. This ratio was 2 to 1, respectively, instead of the usual 1 to 1 ratio obtained in the absence of $Cp(CO)_3W$-H.



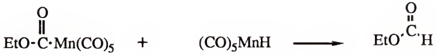
51

2 : 1

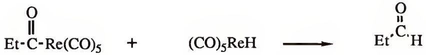
The mechanism of aldehyde or alkane formation from reactions of metal hydrides and metal acyl or alkyl complexes is thought to occur by nucleophylic attack of the M-H bond onto an unsaturated site.(28)



There are many examples of aldehyde formation from the reactions of metal acyls with metal hydrides. These reactions are believed to occur by oxidative addition of metal hydride to the unsaturated acyl complex, followed by reductive elimination of organic aldehyde.(29,30) These conclusions are based on kinetic studies. Two such examples are shown below. Rhenium is also a group 8 metal, but is a row 3, whereas manganese is a row 1 metal.



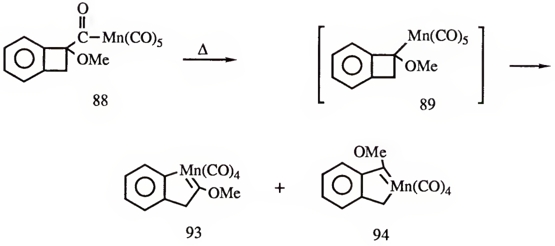
$$\mathrm{EtO{-}C({=}O){-}Mn(CO)_5} \;+\; \mathrm{(CO)_5MnH} \longrightarrow \mathrm{EtO{-}C({=}O){-}H}$$



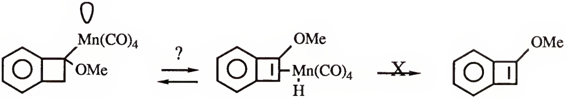
$$\mathrm{Et{-}C({=}O){-}Re(CO)_5} \;+\; \mathrm{(CO)_5ReH} \longrightarrow \mathrm{Et{-}C({=}O){-}H}$$

The preceeding discussion has presented good experimental evidence for a non-radical decomposition of 51. All the products formed in this decomposition can be the result of well known reactions available to organometallic complexes.

One especially convincing piece of evidence for the mechanistic scheme depicted in Figure 1 is given by the thermal rearrangement of acyl 88. This manganese acyl complex was recently prepared by S. Tivakornpannarai(31) of our research group, after the experimental results obtained with the title compound.



Acyl 88 is proposed to form alkyl complex 89 by an alkyl migration. Complex 89 has beta-hydrogens, but the anti-aromaticity and great strain energy that would exist in uncomplexed 92 are a deterent to its formation.



90 91 92

Even though the pi-hydride complex 91 may be formed, the build-up of carbenes 93 and 94 occurs because the benzocyclobutene ligand remains pi-complexed. Once 91 is formed, the back-reaction of 91 to 90 could occur, followed by irreversible ring expansion to form the isomeric carbene complexes 93 and 94.

Another distinct mechanistic possibility for the degradation of 51 involves free radical reactions. It is quite unlikely that this mode of degradation is occurring because of the reasons discussed below. The scheme is shown in Figure 2.

Since metal-acyl bond homolysis is known to occur in some manganese acyl complexes, this mechanistic possibility must be discussed. But what can be disputed is the formation of aldehyde 57, from the acyl radical 98. This acyl radical is expected to rapidly decarbonylate to the methoxycyclobutane radical 99.

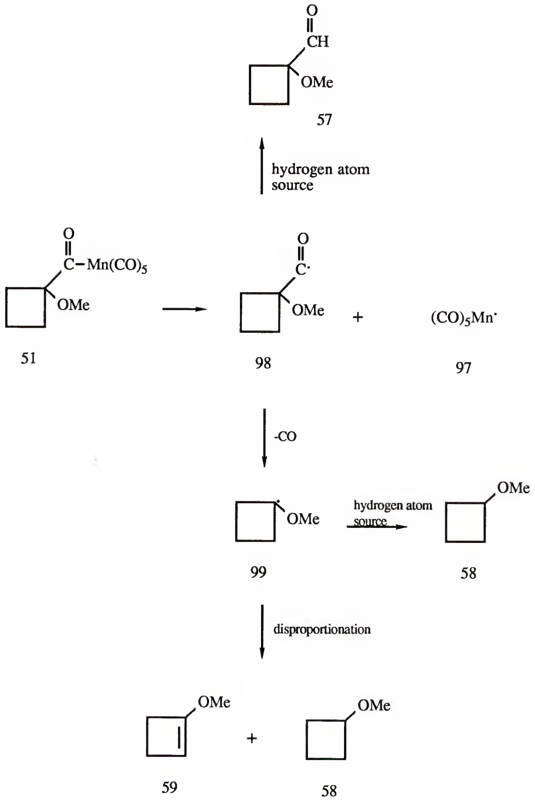
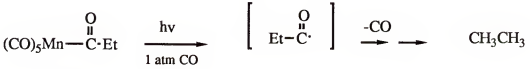


Figure 2. Radical decomposition of 51.

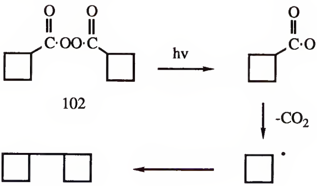
Other workers have found that under conditions of metal-acyl bond cleavage, no aldehyde was detected. Rausch(4) reported the photolysis of 100, under 1 atm CO, resulted in the exclusive formation of ethane. This indicates rapid loss of CO from the acyl radical 101. Radical 101 should lose CO more slowly than 89, because the radical 99 would be stabilized by the adjacent methoxy group. If no propanal is formed via hydrogen abstraction by 101, it is highly unlikely that aldehyde 57 forms as a result of hydrogen abstaction by 98.



100 101

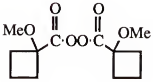
The free-radical mechanism can be further criticized because of an organic product that is not formed, the dimer 72. As shown in Figure 2, at least 50% of the acyl radical is converted to alpha-methoxycyclobutyl radical 99. Some organic dimer 72 should have formed as a result of radical dimerization.

The cyclobutane radical was found to dimerize when generated under photolytic conditions.(32)



102

An attempt was made to synthesize the acyl peroxide 104, in order to generate the alpha-methoxycyclobutyl radical 99. In our hands compound 104 was not obtained. In order to test for correct synthetic procedure, compound 102 was synthesized according to reference 32. The compound could be made quite pure. It was photolyzed in d_6-benzene to observe its free-radical chemistry. It behaved as previously reported.

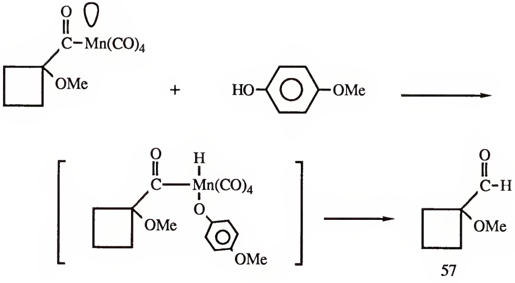


104

Radical trapping experiments were also conducted on acyl 51. In these experiments, up to 20 equivalents of a hydrogen source were heated with 51, at 55° C in d_6-benzene. Two different traps were used; they were paramethoxyphenol and 1,4-cyclohexadiene.

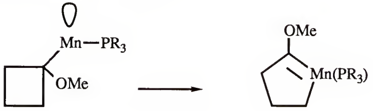
The use of 1,4-cyclohexadiene had no effect on the decomposition of 51. The same three organic products were formed in the same ratios as in the thermolysis of 51.

The results from thermolysis of 51 with paramethoxyphenol, however, were quite different. Only alpha-methoxycyclobutane aldehyde 57 was formed. An explanation of this curious result could be the oxidative addition of the phenol to the unsaturated acyl complex 52. This is followed by reductive elimination to form 57.

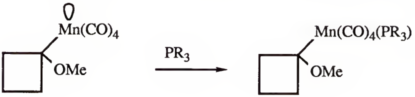


Phosphine-Substituted Complexes of (51)

Phosphine ligands are known to stabilize organometallic complexes.(33,34) One purpose of synthesizing phosphine-sustituted acyls of 51 was to stabilize the carbene complex 56, which could form as shown below. This assumed the PR_3 ligand remained coordinated to manganese throughout the rearrangement.



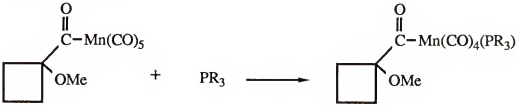
Another purpose of using phosphine ligands was their trapping ability. Perhaps they could provide a mechanistic probe into the decomposition of 51. The unsaturated alkyl complex 54 could be trapped to form the phosphine-sustituted alkyl complex 105. This was tested by decarbonylating 51 in the presence of phosphine. As discussed earlier, the only intermediate trapped was the unsaturated acyl 52. The possibility of trapping 54 existed when $P(Ph)_3$ was used, since some 51 decomposed to organic products. However, no complex such as 105 was detected.



54

105

One of the terminal carbonyls of acyl complex 51 can be displaced via a thermal reaction of 51 with one equivalent of PR_3.



51

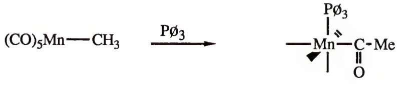
51

106: R=Ø
107: R=Et

Both cis and trans isomers were formed when $P(Ph)_3$ was used. The mixture of isomers exhibited two separate acyl-carbonyl resonances in its ^{13}C spectrum. When triethylphosphine was used, only one isomer was formed; complex 107. The geometrical configuration for 107 was determined by comparison of its IR and ^{13}C spectrum with known compounds. Based on the following observations, it was assigned to have a cis configuration.

The IR spectrum of 107 was taken in CCl_4 solution. Four terminal CO stretches were observed. Other cis

$(PR_3)(CO)_4MnCOR$ complexes exhibit 4 IR absorbances due to the terminal CO ligands.(35) Furthermore, the coupling constant ($^{13}C-^{31}P$) from the acyl-carbonyl ^{13}C resonance of cis $P(Ph)_3(CO)_4MnCOMe$ was also used for confirmation. Since this coupling constant had not been reported in the literature, it was necessary to synthesize 108 and characterize it by ^{13}C NMR. In the induced alkyl migration, only the cis isomer was formed.(35)



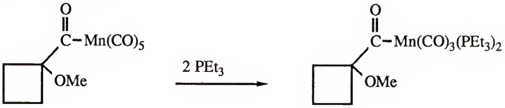
cis 108

In d_6-benzene and at 25 MHz, the coupling constant was determined to be 14.8 Hz. The acyl-carbonyl resonance appeared as a doublet at 266.11 and 265.52 ppm. These values correlate well with those of 107; resonances at 272.74 and 272.15 with a coupling constant of 14.8 Hz.

The cis and trans isomers of the $P(Ph)_3$-substituted acyl of 51 each displayed an acyl-carbonyl resonance. The larger of the two appeared as a doublet at 272.44 and 271.86 ppm with a coupling constant of 14.5 Hz. Thus the major isomer was the cis $P(Ph)_3$-substituted acyl of 51. The smaller acyl resonance appeared as a broad singlet at 264.4 ppm. The coupling constant could not be determined. The minor isomer was assigned a trans configuration.

The cis and trans isomers of 106 could not be separated by column chromatography techniques. They were used as the mixture in the subsequent photolytic and thermal reactions.

When two or more equivalents of PEt_3 were used, the disubstituted phosphine acyl 109 was formed in addition to 107. Increasing the equivalents of $P(Ph)_3$ did not result in a disubstituted acyl. Only mono-substituted cis and trans 106 were formed.



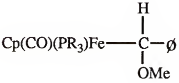
51

109

Attempts to decarbonylate 107 or 109 by either thermal or photolytic means were unsuccessful. This stability can be attributed to the greater degree of metal-ligand backbonding experienced by terminal CO's when electron-donating phosphines are present.(34,36) The result is that the metal-CO bond is stronger and more difficult to remove.

Decarbonylation was achieved in the thermolysis of 106. This required long reaction times (6 days) and a temperature of 65° C. The ubiquitous three organic products were detected, but their ratios were not determined because of the extreme reaction conditions. No new organometallic products were detected. Both $(CO)_{10}Mn_2$ and $(P(Ph)_3)_2(CO)_8Mn_2$ were detected by TLC.

Two factors could be responsible for the decomposition of 106, assuming CO dissociation. Triphenylphosphine is a poorer electron-donor than PEt_3. A smaller degree of back-bonding would result in more labile CO's. Triphenylphosphine is also larger than PEt_3. Crowding about manganese could provide an incentive for CO dissociation. The decomposition of 106 could also be explained by initial $P(Ph)_3$ dissociation. Brookhardt has found that $P(Ph)_3$ dissociates from $CpCOPR_3FeCHPhOMe$, whereas PEt_3 does not.(37) The difference must be the poorer ligand ability of $P(Ph)_3$.



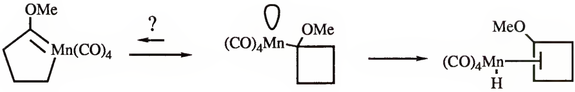
$$\mathrm{Cp(CO)(PR_3)Fe{-\!\!-}\overset{H}{\underset{OMe}{C}}{-}\varnothing}$$

In summation, good evidence has been presented which shows that the unsaturated alkyl complex 54 is a viable species in the decomposition of acyl complex 51. The rearrangement to the carbene complex 56 may be occuring, but there is not a favorable equilibrium. Obviously, the electronic and/or steric situation in the analogous Fp cyclobutyl system 42, which forms the cyclic carbene complex 43, is lacking in the $(CO)_5Mn$ system. The net reaction for the $(CO)_5Mn$-system is beta-hydride elimination in 54, which results in decomposition of 51 by the series of reactions shown in Figure 1.

CHAPTER III

ALPHA-ALKOXYCYCLOPROPYL MANGANESE ACYLS

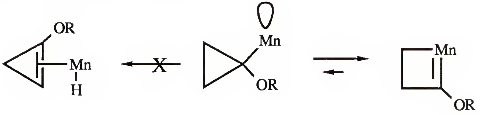
As discussed in Chapter II, the obstacle to carbene complex 60 formation was the facility with which 52 underwent beta-hydride elimination.



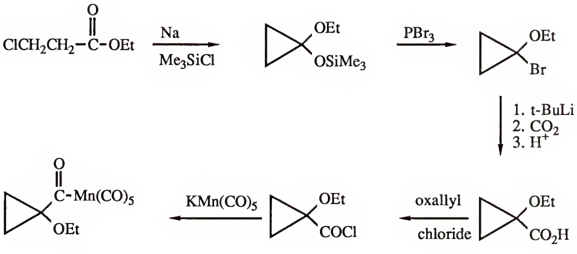
60 52 55

The strain energy difference between cyclobutene (30.6 kcal/mol) and cyclobutane (27.4 kcal/mol) is quite small.(11) Applying this analogy to 52 and 55, it is reasonable that the methoxycyclobutene should form and be stable enough to exist as uncomplexed methoxycyclobutene.

In extending this approach to determine the capability of the next smaller homologue, the cyclopropyl system, to undergo beta-hydride elimination; a different conclusion is obtained. The strain energy of cyclopropane is 28.3 kcal/mol and that of cyclopropene is 54.5 kcal/mol.(11) The higher strain energy of cyclopropene suggests a higher energy barrier for its formation. This could either block the beta-hydride elimination or at least prevent its decomplexation from the metal system if the pi-hydride complex was formed. Assuming no other competitive rearrangements, then perhaps rearrangement to a carbene complex would be favored.



With this in mind, an appropriately alpha-substituted cyclopropylmanganese acyl complex was sought. Thus, alpha-ethoxycyclopropanecarboxylic acid chloride was prepared and metallated with pentacarbonylmanganese.(38,39)



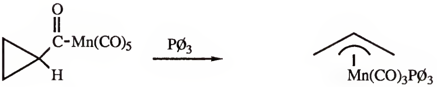
110

The purity of 110 was found to be inconsistent under identical reaction conditions. Varying amounts of unidentified organic compounds were formed in addition to 110. These were found to co-chromatograph with 110 on either silica gel or neutral or basic alumina. A reasonable method of purification was achieved by several recrystallizations from hexane at -30° C.

The acyl complex 110 was subjected to the usual method of decarbonylation; thermolysis at 55° C in d_6-benzene. No decarbonylation was observed and the complex was found to be completely inert under these conditions. Other deuterated solvents such as acetone, CD_3CN and THF were used and gave identical results. The temperatures employed did not exceed 75° C.

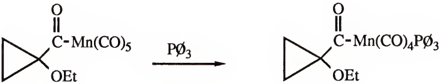
Photolysis with a pyrex filter at room temperature was performed in the aforementioned solvents, and again 110 was determined to be inert to decarbonylation under these conditions. A quartz filter, which allowed for wavelengths as low as 194 nm(40) to be emitted, was similarily employed for decarbonylation. With this method, a very slight evolution of gas was observed at the beginning of the photolysis, but this ceased after a few hours. Via ^{13}C analysis, the acyl 110 appeared totally unchanged and no new products were detected. This inert condition of 110 remained unchanged for up to 7 days of continued photolysis.

The remarkable stability of 110 is quite similar to that of Stone's cyclopropyl acyl complex 111.(41) Decarbonylation was attempted by both thermal and photolytic methods, but 111 was found to be stable. However, he was able to convert 111 into the n^3-allyl complex 112 by refluxing it with $P(Ph)_3$ in cyclohexane. The result of subjecting 110 to these same reaction conditions was the formation of cis- and trans-triphenylphosphine-substituted acyls. No other new products were detected such as the pi-allyl complex corresponding to 112.



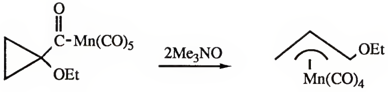
111

112



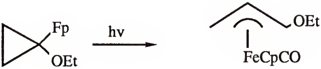
110

Acyl complex 110 was found to undergo reaction with the chemical decarbonylation reagent Me_3NO, in CD_3CN. An excess of 2 equivalents were required for the complete consumption of 110. The reaction produced a single characterizable product; the terminally substituted n^3-allyl complex 113. The yield of 113 was quite low as intractable orange solids were also formed.



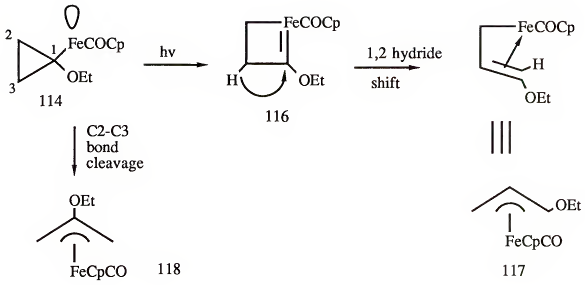
110 113

The terminal substitution pattern of 113 is analogous to that of 117, obtained as one of the products from the photolysis of 114.(42)

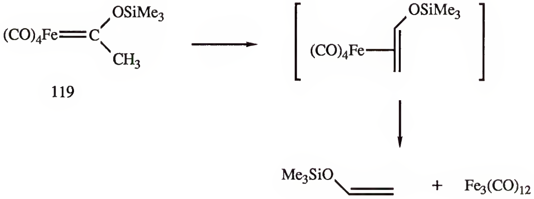


114 117 (~2%)

Complex 117 was proposed to be the result of a 1,2-hydride shift in the metallacyclic carbene complex 116. The best experimental evidence for this originates from monitoring the thermal chemistry of 116 by ^{13}C NMR. A small quantity of 116 was generated in situ during the photolysis of 114 and then heated at 75° C for one hour. The two allylic complexes, 117 and 118, increased in intensity at the expense of 116.



Fortunately, there is also literary precedent for the 1,2-hydride shift proposed for the conversion of 116 to 117. Neutral carbene complexes have been observed to rearrange to pi-bonded alkene complexes or to decomplex to give free alkenes.(43,44)



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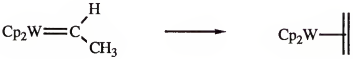


120 121

Assuming the 1,2-hydride shift to be operative, then 113 is evidence for the first non-iron carbene formed as a result of an alpha-alkyl migration from carbon to metal. The absence of any acyl carbene complex 125 is most likely due to the lack of CO in solution. (Another possibility could be that the cyclic carbene complex 124 may have been oxidized by Me_3NO before rearranging by the proposed 1,2-hydride shift(45)). Trimethylamine oxide creates the necessary unsaturated site on manganese, but in the process terminal CO's are converted to CO_2. External ligands such as CO and PR_3 are known to promote alkyl migration. The only ligand present under Me_3NO reaction conditions was Me_3N, and to the author's knowledge no incidence of alkyl migration induced by the presence of amines is known. The overall mechanistic scheme for formation of 113 is shown in Figure 3.

It is interesting that the 2-substituted allyl complex 126 was absent from the reaction of Me_3NO with acyl complex 110. The analogous centrally substituted pi-allyl complex 118 was formed, as a minor product, during the photolysis of 114. This centrally-substituted pi-allyl complex could have resulted from cleavage of the C2-C3 cyclopropyl sigma bond. Experimental work carried out in this lab has shown this C2-C3 cleavage to be a slow process. (This will be discussed in more detail in Chapter IV). It is reasonable that C2-C3 bond cleavage was not competitive with alpha-alkyl migration to form 124.

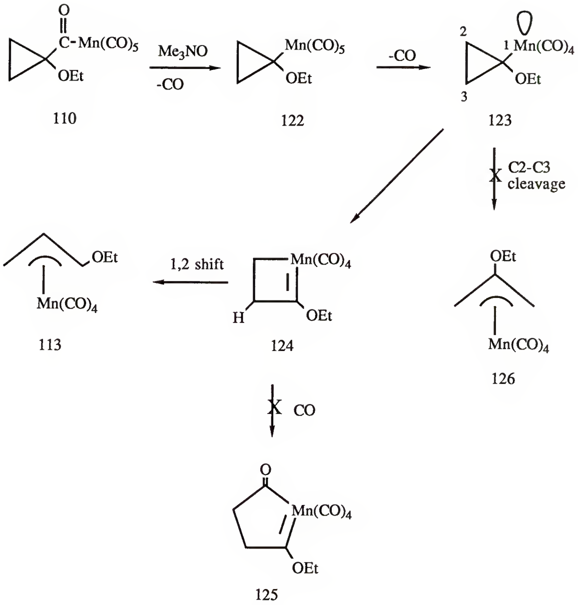
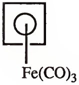
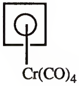
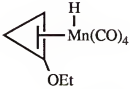


Figure 3. "Carbene" mechanism for formation of 113.

A semi-quantitative argument was presented at the beginning of this chapter, which discriminated against formation of a cyclopropenyl complex 127 due to the high strain energy inherent in such. It is known that highly strained alkenes can form isolable complexes with transition metals. Without complexation to the metal the free alkene would not survive. For example, cyclobutadiene is destabilized by a combination of strain energy (35 kcal/mol) and antiaromaticity (20 kcal/mol), and can only be observed in matrices at low temperatures.(11) Yet, several metal complexes of cyclobutadiene are stable at room temperature.(46,47)







127

The inference is that 127 could be a viable species. Consideration of this begets an alternate mechanism to explain the formation of the terminally-substituted complex 113. Complex 127 is a key species in this scheme shown in Figure 4. Ethoxy-cyclopropene remains pi-bonded to manganese and can add "H" at either C1, to form 123, or at C2, to form the new alkyl complex 130. The steric congestion experienced by the 3^{o} alkyl complex 123 would be somewhat relieved by rearrangement to 130. Unsaturated complex 130 could then rearrange to a saturated pi-allyl complex by cleavage of the C1-C3 cyclopropyl bond. The perplexing feature of this mechanism is the lack of formation of any 126. Is it reasonable to assume that cyclopropyl bond cleavage occurs only with 130 and not with 123 ? This condition might be met if beta-hydride elimination was more rapid than cyclopropyl bond cleavage. As discussed earlier, cyclopropyl bond cleavage is slow, therefore, a method of discernment was required.

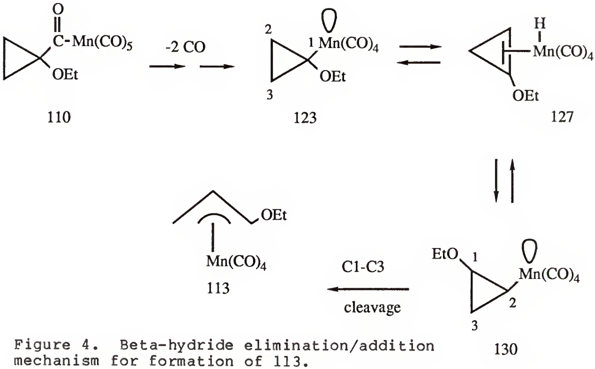
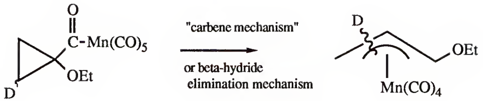
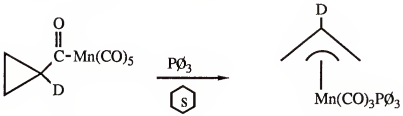


Figure 4. Beta-hydride elimination/addition mechanism for formation of 113.

In order to distinguish between the two mechanisms presented, a properly labeled manganese acyl complex was sought. Deuterium incorporated at the beta carbon of 123 would not be of use in the discernment of these mechanisms. In either, a beta-hydride can be transferred to the ethoxy-substituted carbon.

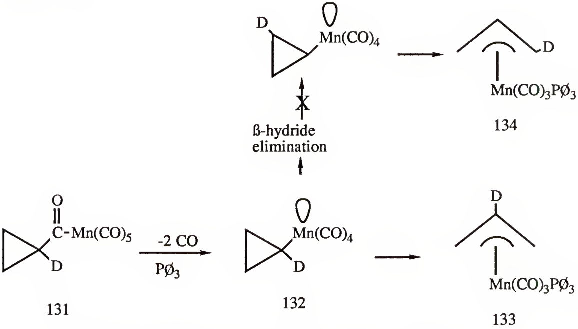


A deuterium label at the alpha carbon would neccesarily replace the ethoxy group and change the unique electronic and also steric makeup of 110. However, this would be of use in gauging the propensity of metal cyclopropyl systems to undergo beta-hydride elimination. Thus the 1-deuterio complex 131 was prepared. Complex 131 was reacted under the conditions described by Stone to generate the pi-allyl complex 112. Based on standard analysis discussed below, only the centrally substituted pi-allyl complex 133 was formed.



131 133

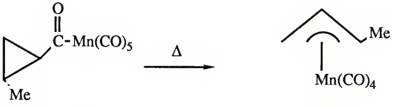
The position of the deuterium in the product would determine the extent of beta-hydride elimination, if any, that occurred in the rearrangement of 131. The propensity of 131 towards beta-hydride elimination could be suggestive of the tendencies of cyclopropyl metal complexes in general to undergo such. If any beta-hydride elimination were occurring, it would be reasonable to assume the formation of some 134. The alpha-alkyl migration that can occur in 123 can be discounted as a possibility for 132 since electron-donating groups at the alpha position are required.



The crude reaction from the P(Ph)$_3$-induced rearrangement of 131 was analyzed by ^{1}H, ^{2}H, and ^{13}C NMR. In the ^{13}C spectrum only one product was suggested; that of the centrally-deuterated allyl complex 133. This was because of a triplet centered at 93.6 ppm, appearing in place of the singlet resonance assigned to the central allylic carbon in the proteated complex 112. Furthermore, only one resonance appeared in the ^{2}H spectrum; at 3.95 ppm. In the ^{1}H NMR of 112, the resonance of the central proton also appears at 3.95 ppm.

Based on these results, it is unlikely that beta-hydride elimination is a viable step in the formation of terminally-substituted ethoxy pi-allyl complex 113.

In addition to 111, Stone had found the analogous pentacarbonylrhenium and the dicarbonylcyclopentadienyliron cyclopropyl acyl complexes to be resistant to thermal or photolytic methods of decarbonylation. It was rather unexpected when the 2-methylcyclopropyl acyl complex 128 was observed to undergo slow, but steady, decarbonylation when heated to 55° C in d_6-benzene.



trans 128 129

It was logical to synthesize an alpha-alkoxycyclopropyl manganese acyl with beta alkyl substituents. Such a complex might undergo thermal decarbonylation and form the appropriate acyl carbene complex. For this reason, the 7-methoxynorcaranylcarboxyllic acid chloride 145 was synthesized according to Figure 5.

Since the analogous iron acyl complex had not been synthesized, it was advantageous to begin work with 146. Acyl complex 146 was synthesized in good yields and found to be a yellow solid. Suitable crystals were grown from dilute hexane solutions and an x-ray was obtained. This is shown in Figure 6. Only one isomer was obtained; that in which the Fp group was trans to the 1- and 6-hydrogens. The carboxyllic acid 144 was obtained as a single isomer. Since the stereochemical integrity of an acid chloride is

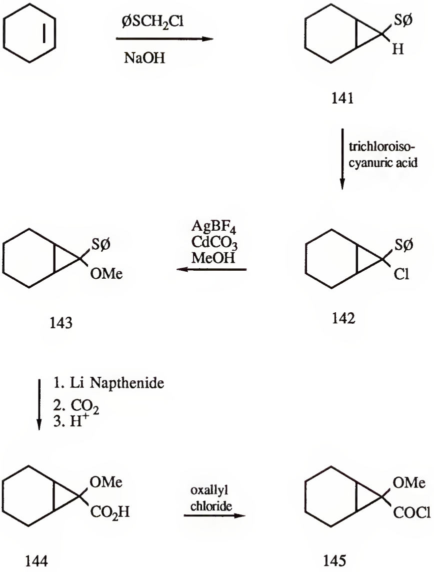


Figure 5. Synthesis of 7-Methoxynorcaranyl,7-carboxylic Acid Chloride.

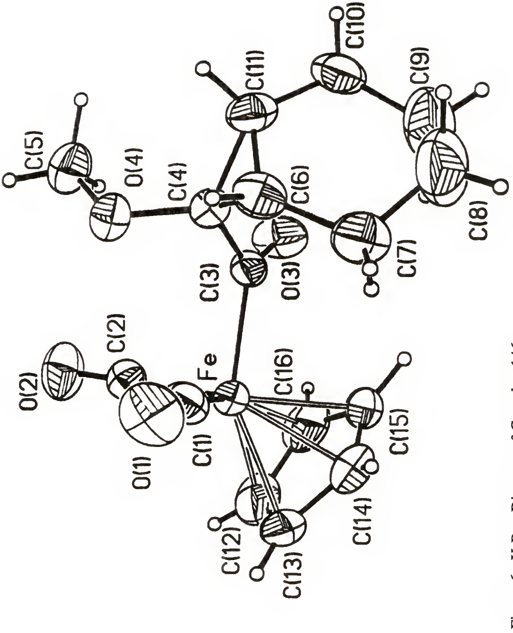
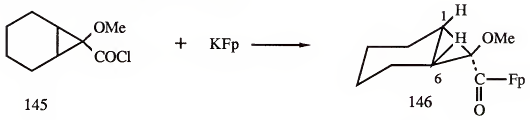


Figure 6. X-Ray Diagram of Complex 146.

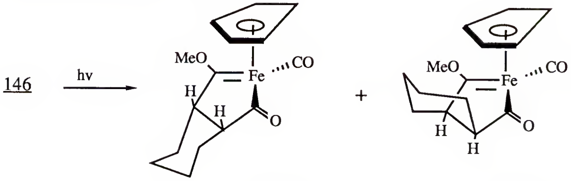
retained in the reaction with a metal anion(48) (and assuming the acid chloride to have the same configuration as the carboxyllic acid), then the carboxyllic acid 144 was obtained as the exo isomer.



145

146

As expected, photolysis of 146 resulted in carbene complex formation. However, there were two isomers of the acyl carbene complex. Fortunately these isomers could be easily separated by column chromatography on silica gel. X-ray quality crystals were grown of each. The major isomer (ca. 66%) precipitated from cold hexane as dark red crystals. The minor isomer was lighter, almost pink in color. The 2 carbene complexes exist in an isomeric relationship because of the orientation of the cyclopentadienyl ring with regard to the cis hydrogens on the C(4)- and C(9)-labeled atoms shown in the x-ray diagrams (Figures 7 and 8).



147 major

anti isomer

148 minor

syn isomer

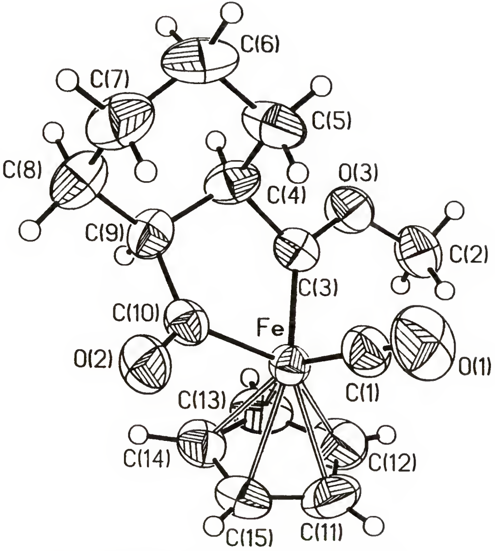


Figure 7. X-ray diagram of the anti bicyclic iron carbene complex 147.

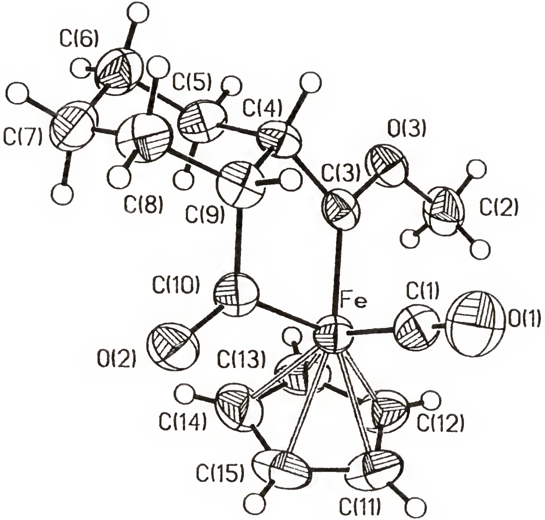


Figure 8. X-ray diagram of the syn bicyclic iron carbene complex 148.

A d_6-benzene solution of the major carbene complex 147 was photolyzed for 12 hrs at room temperature. Analysis by ^{13}C NMR showed partial conversion to the minor isomer 148. The ratio was approximately 70/30 of the 147/148 mixture.

The same conversion was seen to occur when a $NaOCD_3/CD_3OH$ solution of 147 was heated at 55° C for 24 hrs. However an acidic solution of 147 in acetic acid/d_6-acetone was not found to isomerize to 148 when heated at 55° C for up to 3 days. The latter result is rather puzzling if the mechanism for isomerization shown in Figure 9 is correct. The most rational explanation is that acetone may coordinate with 149, therefore blocking alkyl migration to 150.

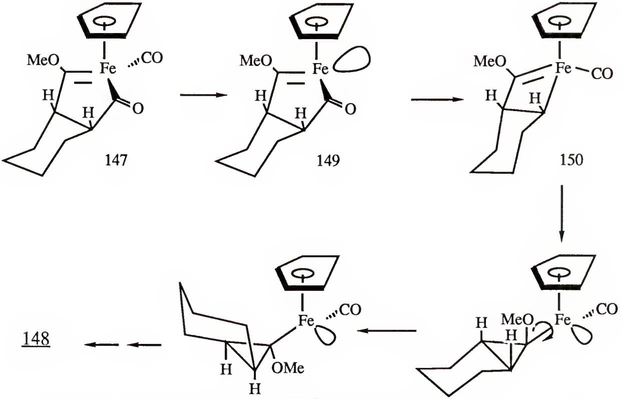
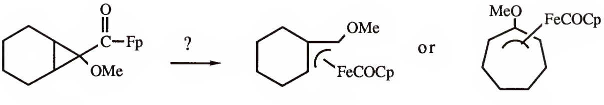


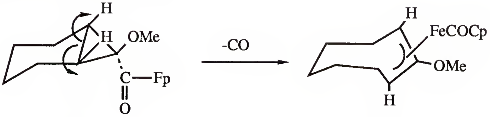
Figure 9. Mechanism of complex 147 isomerization to complex 148.

During the photolysis of 146, only a trace of an "allyl" complex was detected. This was based on the appearance of a ^{13}C resonance at 79.6 ppm. The Cp resonance of exo allyl complexes typically occurs about this value.



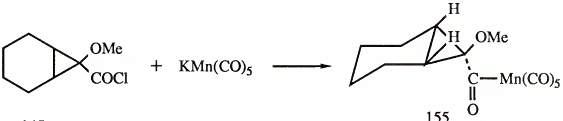
146 153 154

The relative amount of this complex remained constant throughout the photolysis (ca. 0.1%), and its structure eluded determination because it could not be isolated by column chromatography techniques. The ^{13}C resonance for the Cp ring of 117 and 118 was found to be coincidental, at 79.8 ppm. Similarily, it was not possible to surmise whether the unknown allyl complex was 1- or 2-methoxy substituted, and either would be possible. The 2-methoxy substituted allyl complex 154 could have been formed as a result of C1-C6 cyclopropane bond cleavage, since the Fe-moiety is situated trans to the C1- and C2-hydrogens. The stereochemical ring opening of such compounds will be the subject of Chapter IV.



146 154

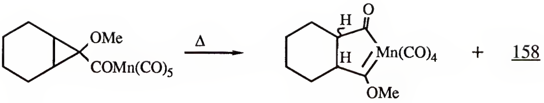
Now that the 7-methoxynorcaranyl system, attached to the Fp moiety, had been observed to rearrange to carbene complexes 147 and 148, it was anticipated that the $Mn(CO)_5$-moiety would behave similarily. Thus acyl complex 155 was synthesized by typical methods. It was found to be a viscous bright yellow oil at room temperature and was observed to precipitate from a hexane solution at -20° C. Even though an x-ray was not obtained, it was assumed that 155 possessed the same stereochemistry as the analogous iron acyl complex 146.



145

155

A solution of 155 in d_6-benzene was heated at 65° C in an oil bath under nitrogen. A slow, steady stream of gas was evolved. By monitoring the reaction by ^{13}C NMR, it was determined that acyl complex 155 was undergoing rearrangement to three new complexes. Two of these were acyl carbene complexes, identified as such from the lowfield resonances at 362 and 357 ppm (major), which are characteristic of carbenic carbons and the new acyl resonances at 269 and 266 ppm. The third new complex was formed in about a 5% relative yield and was not identified at the time of this writing.



155

156, 157

Attempts at separation of complexes 156, 157, and 158 via column chromatograpy were unsuccessful (silica gel, alumina) as all three complexes were found to co-chromatograph. Of these three complexes, the unknown complex 158 was the most stable when prolonged thermolysis was employed. The two carbene complexes disappeared, and new vinyllic resonances appeared in the ^{13}C spectrum. It is reasonable to assume that 156 and 157 decomposed to these vinyllic compounds.

The fine structural details of carbene complexes 156 and 157 cannot be discussed with any certainty since no x-rays were obtained at the time of this writing. The major carbene could be "selectively" recrystallized from a diethyl ether/hexane solution, cooled to -30° C, as needle-like bright yellow crystals. These will be submitted for x-ray analysis. The most resonable structures are shown above in which the 1- and 6-hydrogens have either a cis or trans relationship to one another.

Because of the symmetry inherent in the Mn(CO)$_4$-moiety, the isomerism of the analogous iron carbene complexes, 147 and 148, is not possible for the proposed structures, 156 and 157. Other less likely possibilities could be the result of different conformations assumed by the cyclohexane ring. This would be highly unusual.

The isomeric nature of 156 and 157 may be interesting, but it is a minor point. The important result is that acyl complex 155 undergoes thermal rearrangement to form acyl carbene complexes because: a) beta-hydride elimination is unaccessible, and b) 2,3-alkyl substitution on the cyclopropyl ring permits decarbonylation by thermal methods.

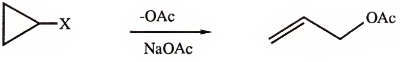
In conclusion, it has been possible to induce alpha-alkyl migration from carbon to metal in a metal system other than the FeCpCO-system. The problem of beta-hydride elimination as a side reaction, was avoided by use of the cyclopropyl system.

CHAPTER IV

STEREOCHEMISTRY OF THE C2-C3 CYCLOPROPYL BOND OPENING OF METAL COMPLEXES

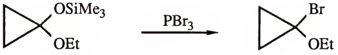
The rearrangements of small ring organic compounds have always attracted attention. One area of considerable interest in the past, has been the rearrangement of cyclopropyl halides or tosylates to allylic compounds under solvolytic conditions. This area of research is of immediate interest to our group.

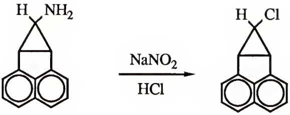
It was found that when cyclopropyl compounds 160 (X = -OTs, Br, Cl) were heated with sodium acetate in acetic acid, the 3-substituted allyl acetate was formed.(49,50)



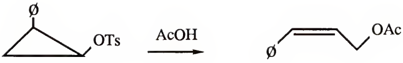
160 161

A direct substitution was obviously not occurring, but is known to occur in some instances, usually when an alpha electron-donating group is present.(39,51)





The solvolysis of 160 involves ring-opening at some point, as well as "displacement" of X. The time of ring-opening became the major point of interest in the published results of many research groups.(52,53,54) Many kinetic studies were performed in order to evaluate whether a cyclopropyl cation were formed first (followed by C2-C3 bond opening), or whether a concerted C2-C3 bond opening occurred to form an allyl cation. The experimental results were consistent with the theoretical predictions of Woodward and Hoffmann involving electrocyclic ring-opening.(55) (The possibility of 2 different modes of disrotatory opening for cyclopropyl cations was noted, and furthermore the correct direction-disrotatory opening, away from the leaving group X, was chosen as the favored process based on calculations.) For example, De Puy et al(52) found that 163 and 164 solvolyze at distinctly different rates; the trans-substituted compound reacts faster.



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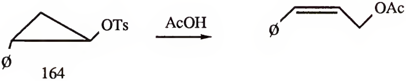
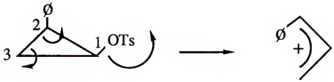
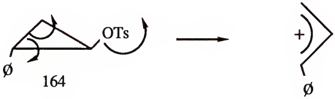


164

Both the cis and trans isomers were found to solvolyze faster than cyclopropyl tosylate. A concerted reaction was postulated in which C2-C3 bond cleavage occurred with breaking of the C1-OTs bond. Furthermore, the C2-C3 bond opened in a disrotatory manner; away from the departing -OTs group, as shown below. This manifested itself in the difference in reaction rates between 163 and 164. Disrotatory ring-opening occurs in the same direction for both, but the trans compound 164 encounters less steric inhibitions resulting in a greater reaction rate.

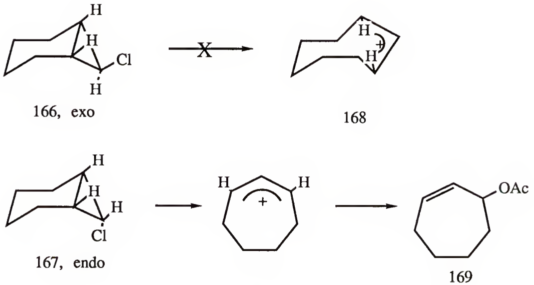


163



164

Although these interpretations are based on kinetic studies, there are other results that have a more concrete stereochemical basis.(53,54) The 7-chloronorcaranes were subjected to solvolysis in acetic acid and only the endo isomer 167 was found to rearrange to the cycloheptenylacetate 169. The exo isomer 166 did not react for up to 692 hrs under these same reaction conditions. The requisite disrotatory mode of opening for 166 would lead to formation of the high energy intermediate 168. Furthermore, 166 did not even react with AgOAc in HOAc for 2 hrs at 200° C.



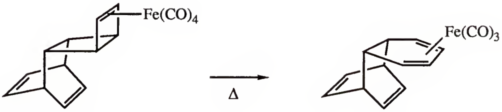
166, exo

168

167, endo

169

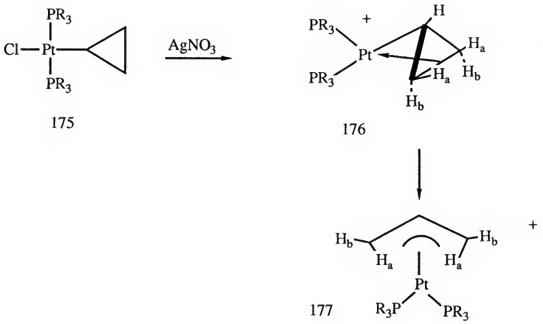
Because our research sometimes involves metals directly bonded to cyclopropyl rings, we became interested in ascertaining the extent of influence a metal exerted on the C2-C3 ring opening. Would the opening follow the rules of orbital symmetry as observed in organic cyclopropyl rearrangements? Or would the metal cause the disfavored mode of opening: a conrotatory one? The cyclobutenyl iron complex 170, studied by Pettit,(56) was found to thermally rearrange to the cyclohexadienyl complex 171 by a disrotatory opening. A conrotatory opening would be expected for the thermal rearrangement of organic cyclobutenyl compounds based on orbital symmetry rules.



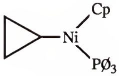
170

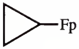
171

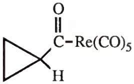
Earlier studies had shown that some metal cyclopropyl complexes could rearrange to pi-allyl complexes.(41,57,58) Puddephatt(57) suggested the platinum cyclopropyl complex 175 rearranged to 177 by insertion of Pt into the C2-C3 bond. Essentially, this rearrangement would involve a disrotatory C2-C3 opening towards the Pt leaving group, just the opposite mode experimentally observed with cyclopropyl halides and tosylates.



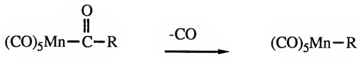
Other cyclopropyl metal sigma complexes, such as 178(59), 179(42) and 180(41), do not undergo rearrangements to pi-allyl complexes under thermal or photochemical conditions.


178


179

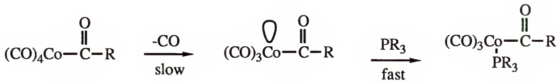

180

It would appear that an unsaturated metal center is required for pi-allyl formation.(60) For 178 or 179, slow loss of CO or PR_3 can be rationalized in terms of the electronegativity of the cyclopropyl ring. Electron-withdrawing groups would be expected to contribute little stability towards an electron-deficient 16-electron intermediate. This rationale could be extended through one bond to include cyclopropyl acyl complexes such as 180. In fact, kinetic studies on the decarbonylation rates of manganese acyls 1, with R varying in electronegativity, were performed.(61) It was found that the more electronegative R was, the slower the rearrangement to the alkyl complex occurred. Another kinetic study on the rate of phosphine-substitution of cobalt acyl complexes showed the same trend, that increased electronegativity for R resulted in slower loss of CO. (This latter reaction was first order in 172 and reaction of 173 with $P(Ph)_3$ was quick.) In addition to an electronic effect, a steric effect was apparent in this study. The larger R was, the faster phosphine-substitution was observed to occur. The two effects were separated.



$$(CO)_5Mn{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow{-CO} (CO)_5Mn{-}R$$

1 2

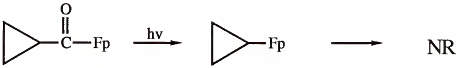


$$(CO)_4Co{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow[\text{slow}]{-CO} (CO)_3Co{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow[\text{fast}]{PR_3} (CO)_3\underset{PR_3}{Co}{-}\overset{O}{\overset{\|}{C}}{-}R$$

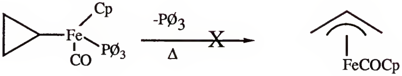
172 173 174

Alpha-substituted cyclopropyl metal systems

When dicarbonyl(cyclopentadienyl)(cyclopropylcarbonyl) iron is photolyzed in d_6-benzene, rearrangement to the alkyl complex occurs.(63) No further rearrangement of the alkyl complex 179 to a pi-allyl complex is observed. If an empty coordination site on the metal is requisite for pi-allyl complex formation, then generation of such a site on 179 should result in the desired pi-allyl complex. Conti(42) had synthesized the triphenylphosphine derivative of 179 since PR$_3$ groups are known to be thermally labile ligands when present on Fp complexes.(37) However, thermolysis of complex 182 did not result in loss of P(Ph)$_3$ and formation of 183. Complex 182 was found to be very stable.

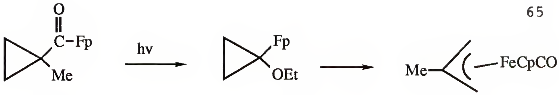


181 179

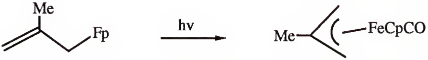


182 183

The alpha-methylcyclopropyl complex 184 was synthesized by standard methods and found to form bright yellow needle-like crystals. Complex 184 was photolyzed with a pyrex filter at room temperature and underwent alkyl migration to form 185. This rearrangement was fairly rapid. Alkyl complex 185 was rather stable, but it slowly rearranged to the pi-allyl complex 186. The identity of 186 was verified by synthesizing it by an alternative literature method.(64)

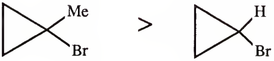


184 185 186

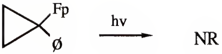


187 186

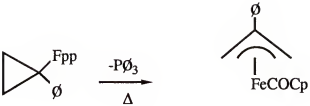
The difference in reactivities between the cyclopropyl Fp complex 179 and the methyl substituted complex 185 is consistent with the difference in the solvolysis of cyclopropyl bromide and alpha-methylcyclopropyl bromide.(65) Roberts et al had found the methyl substituted compound to solvolyze 40 times as fast as cyclopropyl bromide.



Trace synthesized the alpha-phenylcyclopropyl Fp complex 187 and found it to be completely inert to photolytic conditions at room temperature.(66) In contrast, the triphenylphosphine-substituted complex 188 was observed to form the 2-substituted pi-allyl complex 189 when heated in d_6-benzene.

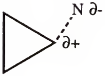


187

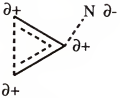


188 189

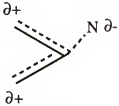
It appears that the more electron-donating substituents promote the C2-C3 ring cleavage and subsequent pi-allyl complex formation. This suggests that C1 develops partial positive charge during the rearrangement and that the transition state could resemble 190 or 191, but not 192.(54) The importance of 190 is diminished by results of the following experiment, which support forms 191 and/or 192 as the more reasonable transition state representation.



190



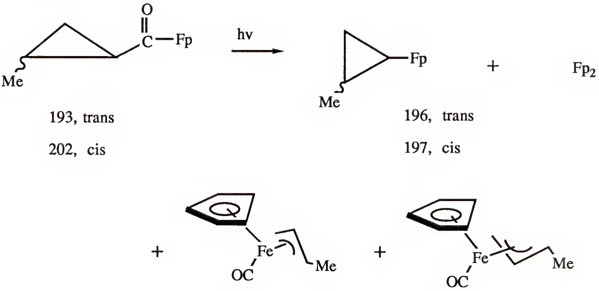
191



192

The 2-methylcyclopropyl Fp acyl complex 193 was synthesized by usual procedures, and was found to be a red-yellow oil. A mixture of isomers was obtained, with the trans isomer predominating.

When an 86/14 ratio of trans/cis 2-methylcyclopropylcarbonyldicarbonylcyclopentadienyliron, 193 is photolysed for 40 hrs at 15° C, a complex mixture of iron-containing products is formed. Foremost among the products are two isomers, the exo,syn and endo,syn crotyl allyl complexes, 194 and 195.



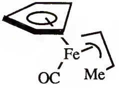
193, trans
202, cis

196, trans
197, cis

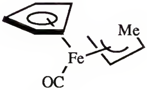
194
exo,syn

195
endo,syn

Other products present in the reaction mixture are (in decreasing amounts) 1) the trans 2-methylcyclopropyl Fp sigma 196, 2) the cis 2-methylcyclopropyl Fp sigma 197, 3) Fp$_2$, and 4) ferrocene. The anti crotyl allyl, with either an exo configuration 198 or an endo one 199, could not be detected in this mixture, either by ^{13}C or ^{1}H NMR.

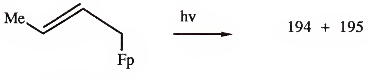


198
exo,anti

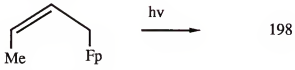


199
endo,anti

In order to verify the identities of 194 and 195 and also to confirm the absence of 198 and 199, the syn and anti crotyl allyls complexes of FeCOCp were synthesized by an alternative manner.(67) A 63/37 mixture of the trans and cis crotyl sigma complexes of Fp, 200 and 201, were photolyzed in d$_6$-benzene at 15° C. The reaction was monitored by ^{13}C NMR spectroscopy and was terminated when the starting sigma complexes were consumed. The reaction was quite clean and produced the corresponding exo,syn and exo,anti pi-allyls in about a 63/37 ratio, respectively. The cis and trans configurations of the methyl group remained stereochemically intact when pi-bonding to the metal. This situation is encountered when the analogous crotyl sigma complexes of pentacarbonylmanganese are chemically decarbonylated with Ir(Diphos)$_2$Cl.(68) This experiment was complicated by the appearance of a third isomer, attributed to the endo,syn crotyl allyl complex 195. The presence of the endo,anti crotyl allyl complex 199 could not be detected. This is not surprising since 199 should be the least stable of the 4 possible isomers.(64)



200, trans

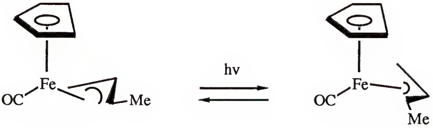


202, cis

Purification of this mixture (194, 195, 198) on either alumina or silica gel resulted in isolation of only the exo,syn complex 194 and the exo,anti pi-allyl complex 198. The endo,syn complex 195 was either isomerized and/or destroyed by the purification process.

The endo,syn isomer 195 could be regenerated by photolysis of the exo,syn/exo,anti allyl complex mixture at 15° C for 5 hrs. It was observed that the relative amount of the exo,syn isomer, in comparison to the exo,anti isomer, decreased with the appearance of the endo,syn isomer. Futhermore, after 36 hrs at room temperature, the endo,syn isomer 195 had essentially disappeared while the exo,syn to exo,anti ratio had increased.

These results imply that the photochemically-generated endo,syn isomer originates from only the exo,syn crotyl allyl complex 194. It is assumed the syn orientation of the methyl group is retained in this transformation based on previous work by Rosenblum.(64)



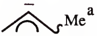
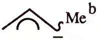
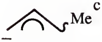
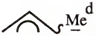
194 195

It was necessary to confirm the origin of 195 since it is produced in the photolysis of 193. There is another condition that must be satisfied before any conclusions can be drawn concerning the stereochemistry of the ring opening of complex 193. The exo,anti complex 198 must be stable under photolytic conditions and not isomerize to the exo,syn complex 194.

For this reason, T1 studies were carried out on a syn/anti crotyl allyl mixture using the standard program employed with the Varian 300XL NMR spectrometer. Unfortunately, the Cp resonance of both exo,syn and exo,anti allyls is coincidental in the ^{13}C spectrum. However, the other 4 allylic carbon resonances of each isomer are well resolved and were all used in the ^{13}C-integrated stability study. After T1 values were obtained for these 8 carbon resonances, a delay time of 15 sec (D1) was deemed appropiate to use for the pulsing sequence. An initial spectrum was quantified after it was determined that an equilibrium value of 195 was obtained, as described below.

When the photolysis of 194 and 198 is carried out at 34° C, instead of 15°C, there is a decrease in the relative amount of endo,syn allyl. At 34° C about 8% of the syn allyl assumes the less thermodynamically stable endo configuration when measured directly after photolysis. At 15° C the amount of endo,syn relative to exo,syn increases to about 30%. Therefore, the initial mixture of crotyl allyls (194 and 198) was photolyzed and monitored for 8 hrs prior to ^{13}C measurements. At this time the amount of 195 was maximized. The syn/anti ratios shown in Table 2 for

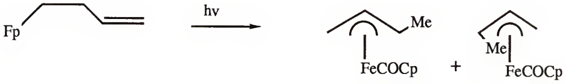
Table 2. Results of the ^{13}C NMR integrated study of the relative amounts of exo,syn to exo,anti subjected to photolysis in d_6-benzene.

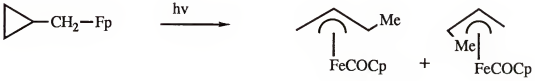
Hours of photolysis at 34° C.	 [a]	 [b]	 [c]	 [d]
8	2.16	2.11	2.00	2.27
24	2.16	2.06	2.07	2.32
48	2.24	2.28	2.09	2.46
72	2.21	2.07	2.02	2.22

[a,b,c,d] these numbers represent ratios of exo,syn to exo,anti determined by the ^{13}C NMR integrated values of the denoted carbons.

the initial mixture thus account for any exo,syn to endo,syn isomerization. The mixture was then photolyzed at 34° C for an additional 72 hrs, with periodic quantification by ^{13}C NMR. The results in Table 2 clearly show that the ratio of syn to anti allyl remains constant. Under photolytic conditions (and a temperature of 34° C), the exo,anti isomer is not converted into the exo,syn isomer.

It is interesting to note that the syn and anti crotyl allyl complexes of FeCOCp have been synthesized by two additional published methods.(69,70) The reactions are shown below. In both preparations it was reported that the same syn/anti ratio of 65/35 was obtained, but neither paper mentions the possibility of exo/endo isomers.

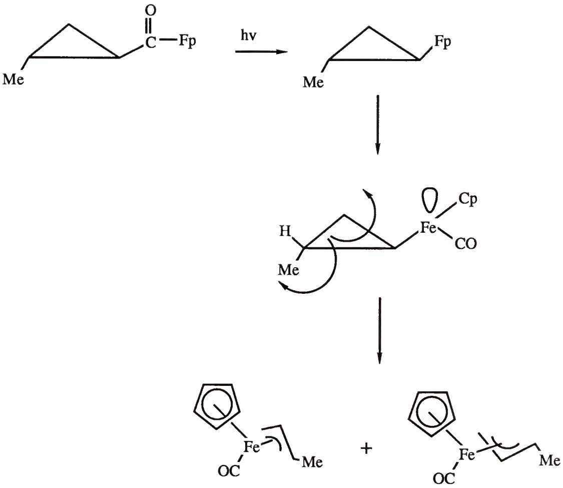




The latter reaction shown above was carried out in our lab using the same experimental conditions as described. Both exo,syn and exo,anti isomers were detected as well as the endo,syn isomer.

The mechanism of cyclopropyl ring opening can now be proposed. The trans 2-methylcyclopropyl acyl 193 decarbonylates and undergoes rearrangement to the trans 2-methylcyclopropyl sigma complex 196. After an unsaturated site is created, by loss of another CO, the C2-C3 bond of the cyclopropane ring opens in a disrotatory mode, away from the iron center. This is depicted in Figure 10. If the C2-C3 bond had opened in a disrotatory fashion towards the iron, the anti allyl would have been formed.

A disrotatory opening, away from the iron, occurring in the unsaturated cis-methyl cyclopropyl sigma intermediate should be disfavored based on steric grounds. Even though the exo,anti isomer is not observed in the photolysis of the 86/14 trans/cis acyl complex mixture, a small amount is observed to form when a 70/30 trans/cis mixture of Fp cyclopropyl sigma complexes is photolyzed for 24 hrs. The 70/30 mixture of Fp sigma complexes was synthesized by the usual method of reacting Fp^- with an isomeric mixture of 2-methylcyclopropyl bromide. Since other workers have found that a mixture of cis/trans alkyl complexes is obtained starting with a single isomer of a 2-substituted cyclopropyl bromide reacting with Fp^-, separation of 206 and 207 was not attempted.(42) The complete synthesis is shown below.



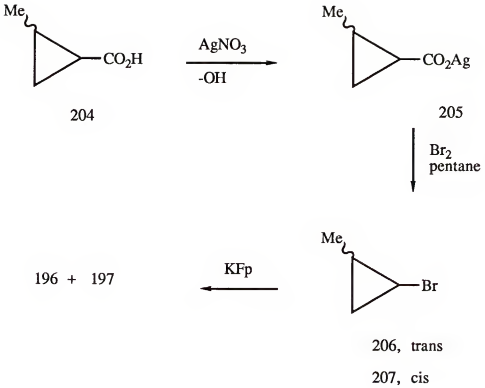
194

exo,syn

195

endo,syn

Figure 10. Mechanism of the C2-C3 cyclopropyl ring-opening for trans-2-methylcyclopropylcarbonyl(dicarbonyl)(cyclopentadienyl)iron.



During the photolysis, the trans-methyl cyclopropyl sigma complex 196 is consumed faster than the cis isomer, and the exo,syn and endo,syn allyl complexes form faster than the exo,anti allyl complex. After 48 hrs of photolysis the ratio of syn/anti was 86/14. The ratio of cis to trans cyclopropyl sigmas complexes, at this time, was roughly 1 to 1. Again, there is precedent in the literature that validates these observations. Cis 2-methylcyclopropyl bromide was found to solvolyze at 1/15th the rate of the corresponding trans isomer.(71) The different rates were ascribed to the greater steric hinderance encountered by the cis isomer during disrotatory ring-opening.

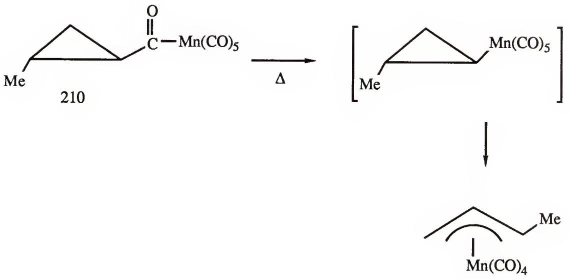
One final experiment was conducted to determine whether the endo,syn and exo,syn allyl complexes were indeed originating directly from the trans alkyl complex

196. This was easily accomplished by photolyzing a mixture of 196 and 197 in the presence of an internal standard; ruthenocene. It was determined that the disappearance of 196 correlated very well with the appearance of 194 and 195. (In other words, the trans isomer 193 was not rearranging to the anti complex 198.)

The following statements summerize all the previous experimental data. The trans acyl complex 193 rearranges to the trans alkyl complex 196. By use of an internal standard, complex 196 was determined to undergo further rearrangement to the exo,syn and endo,syn pi-allyl complexes, 194 and 195. The cis alkyl complex 197 undergoes a slower rearrangement (than the trans isomer) to the exo,anti pi-allyl complex 198. This is most likely the result of greater steric hinderance. The exo,anti complex 198 does not isomerize to the exo,syn or endo,syn complex. The endo,syn complex 195 is formed from the exo,syn complex 194 by photolysis, and the endo,anti complex 199 is never observed.

From these experiments, it can be concluded that the C2-C3 bond cleavage occurs by a disrotatory opening, away from the iron moiety. This is the same situation encountered in the organic cyclopropyl systems discussed previously. It cannot be determined whether the iron exerts any influence at all since a different mode of ring-opening was not observed. Carpenter has found similar results in the thermal rearrangement of a methylenecyclopropane iron complex to a trimethylenemethane complex.(72)

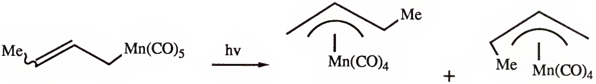
The analogous pentacarbonylmanganese acyl complex 210 was synthesized. Only the trans isomer was obtained. Complex 210 is fairly soluble in d_6-benzene at room temperature. A saturated solution of 210 in d_6-benzene was heated at 55° C under N_2. A very slow evolution of gas was observed. Via NMR techniques, it was evident that rearrangement to the pi-allyl complex 211 was occurring. The transient sigma complex could not be detected. For 0.34 g of 210 (0.11 mmol) in 0.8 ml d_6-benzene, it was necessary to continue thermolysis for 7 days to completely decompose 210. Only the syn isomer 211 was detected. Verification of the identity of 211 was easily achieved since both the syn and anti crotyl allyl complexes of $(CO)_5Mn$ have long been known.(73,74)



210

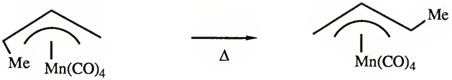
211

The stereochemistry of the C2-C3 ring-opening in 210 could not be determined from this experiment. An 84/16 mixture of anti/syn crotyl allyl complexes was obtained by the photolysis of the corresponding sigma complexes in d_6-benzene at 15° C.



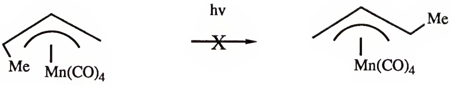
211, syn   212, anti

When this mixture was heated to 65° C in an oil bath under N_2, complete isomerization of the anti complex 212 to syn complex 211 occurred within 24 hrs.



212, anti   211, syn

However, this same mixture was found to be stable to photolytic conditions (d_6-benzene or CD_3CN), with either a pyrex or quartz filter. As in the manner described previously for the analogous iron complexes, it was determined that the anti allyl complex 212 did not isomerize to the syn allyl complex 211 under photolytic conditions at 15° C.



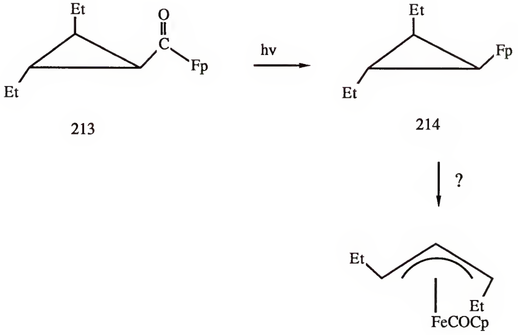
212, anti   211, syn

Photolysis of 210 in either d$_6$-benzene or CD$_3$CN with a pyrex filter did not result in decarbonylation. By using a quartz filter, decarbonylation of 210 was possible even though it was qualitatively much slower than the thermolysis. Photolysis with quartz was performed at 15° C in both solvents. The relative slowness of the reaction may have been due to the limited solubility of 210 in these solvents at 15° C. Photolysis was continued for 72 hrs and a 5% yield of the syn complex 211 was detected by ^{13}C NMR. The anti isomer was not detected. It should be noted that the formation of 212 was not anticipated.

Based on these rather limited experiments, the (CO)$_5$Mn-moiety appears to exert the same influence as the Cp(CO)$_2$Fe-system on the C2-C3 cyclopropyl mode of ring-opening in the complex 210.

The slower photolysis of the cis 2-methylcyclopropyl Fp alkyl complex 197 in comparison to the trans isomer 196 was attributed to sterics. A more dramatic case involving steric inhibition of the C2-C3 bond opening is observed in the photolysis of the trans 2,3-diethylcyclopropyl Fp acyl complex 213 in d$_6$-benzene at room temperature. The alkyl complex 214 is readily formed. Only a very small amount (ca

1%) of a compound displaying a resonance at 79.5 ppm was formed. The Cp ring-resonance of exo allyl complexes of FeCOCp appears in this region. The small amount of 215 prevented further characterization. Prolonged irradiation times did not result in a further increase in the amount of 215. Because there were 7 other new discernable resonances in the ^{13}C spectum, the compound is most likely the unsymmetrical syn,anti allyl complex shown. This would correspond to a dirotatory mode of C2-C3 bond opening, away from iron, as found for complex 193. The symmetrical syn,syn allyl would exhibit only 4 other resonances. The latter isomer would form as a result of conrotatory C2-C3 bond opening.



213

214

215

CHAPTER V

CONCLUSIONS

In order to observe the alpha-alkyl migration from carbon to metal (forming a metal carbene complex) in the pentacarbonylmanganese system, the beta-hydride elimination mechanism had to be suppressed.

This was accomplished by synthesis of an alpha-alkoxy-cyclopropyl manganese acyl with 2,3-alkyl substituents. The specific complex was 155. Thermolysis of this acyl complex gave two acyl carbene complexes. The structures have thus far eluded determination.

Also, the stereochemistry of the C2-C3 ring-opening in cyclopropyl alkyl complexes was determined. The bond breaking occurs in a disrotatory manner away from the metal center.

CHAPTER VI

EXPERIMENTAL

General

All the solvents used were reagent grade. Both THF and diethyl ether were dried and deoxygenated by distillation over Na-K amalgam. Benzene was dried by distillation over P_2O_5. Those solvents used for column chromatography and or extraction/filtration were degassed by passing nitrogen through for one hour. The alumina used for chromatography was Fischer certified neutral and was degassed on a vacuum line for 12 hours prior to use. The silica gel used was Alpha Products, 59 micron pore size, and was degassed on the vacuum line for 12 hours before use. Synthesis of all organometallic compounds was performed on a high vacuum line under a nitrogen atmosphere. Other manipulations were performed in a glove box under a nitrogen atmosphere. Microanalysis was performed by Atlanta Microlabs or the microanalytical laboratory of this department. Mass spectral analysis was performed by this department. Proton and carbon NMR spectra were measured on either a JEOL 100FX or Varian 300FX. All infrared spectra were recorded on either a Perkin Elmer 137 or a Perkin Elmer 1640 spectrometer. Melting points were determined on a Thomas Hoover melting point apparatus.

Synthesis of Alpha-methoxycyclobutylcarbonyl(pentacarbonyl)manganese (53)

Potassium pentacarbonylmanganese was prepared by the method of Gladysz.[75] To a slurry of 4.5g freshly prepared $KMn(CO)_5$ (19.4 mmol) in 30 ml THF at 0° C was slowly added 3.2 g (19.4 mmol) alpha-methoxycyclobutylcarbonyl chloride[17] in 20 ml of THF, also at 0° C. A double-ended cannula was used for the addition of the acid chloride. The reaction was allowed to stir for 24 hours, while warming to room temperature, then the solvents were removed on line. The resulting orange-yellow residue was extracted several times with 70 ml hexane, filtered over celite and rotovaped to yield an oil. Flash chromatography on silica gel with 15/85 ethyl acetate/hexane as eluent brought down the desired acyl as a yellow band. After removal of solvents, 3.7 g (62%) of a yellow, air-sensitive oil was isolated. CHN analysis for $C_{11}H_9O_7Mn$; Calculated: C, 42.87; H, 2.93; Found: C, 42.90. H, 2.91. MS (CI): 309 (M+1), 281 (M+1 - CO). ^1H NMR ($CDCl_3$, 100 MHz): 1.1-2.3 ppm (mult, 6H, ring-CH_2's); 3.4 (s, 3H, OMe).^{13}C NMR (d_6-acetone): 259.8 ppm (acyl CO); 211.9 (M-CO); 94.1 (alpha-ring C); 51.9 (MeO); 28.3 (beta-ring C's); 12.3 (gamma-ring C). IR (CCL_4): 2112.3 cm^{-1}, 2046.8 (m); 2017.5, 2007.0 (vs); 1645.8.

Thermolysis of Alpha-methoxycyclobutylcarbonyl(pentacarbonyl)manganese (53)

In a typical experiment, 0.3 g 53 (0.97 mmol) and .7 ml d_6-benzene were charged into an 5 mm NMR tube with a graphite boiling chip. The tube was immersed in an oil bath at a temperature of 62-65° C and maintained under a nitrogen atmosphere. Decarbonylation was immediate, but rather slow. The experiment was allowed to run for 15 hours. The volatiles from the reaction were vacuum-transfered and a ^1H NMR spectrum taken and integrated for relative amounts of organic products, 57, 58, and 59. The results are listed in Table 1. The non-volatiles were examined by ^1H and ^{13}C NMR, which showed that only unreacted acyl, 53 remained. Also present in the non-volatiles was $Mn_2(CO)_{10}$, detected by TLC and IR. The thermolysis of 53 was also carried out in d_8-toluene, at 55° C. The relative ratios of organic products are listed in Table 1. A solution of 0.3 g 53, 0.1 g napthalene and 0.8 ml d_6-benzene was analyzed by quantitative ^{13}C NMR for the initial ratio of 53 ($-OCH_3$ resonance at 50.8 ppm) to napthalene (125.9 ppm). The solution was heated at 52° C for 36 hrs, and the crude reaction was then analyzed by quantitative ^{13}C NMR. The ratio of the sum of unreacted 53 plus 57 ($-OCH_3$) plus 59 ($-OCH_3$), (no 58 could be detected) to napthalene was 95% of the original value. This means that only about 5% of 53 could not be accounted for in the thermal degradation of 53.

Photolysis of Alpha-methoxycyclobutylcarbonyl(pentacarbonyl)manganese (53)

Photolysis was carried out using a water-cooled Hanovia lamp with a Pyrex filter. An NMR tube was charged with 0.3 g 53 and .7 ml d_6-benzene and subjected to photolysis in a water bath at 25° C. Decarbonylation proceeded very slowly and it was necessary to run the reaction for 48 hours. The volatiles were transferred by a bulb to bulb distillation and analyzed by ^1H NMR; the results appear in Table 1. Analysis of the non-volatiles showed only unreacted 53 and $Mn_2(CO)_{10}$ were present.

Reaction of Alpha-methoxycyclobutylcarbonyl(pentacarbonyl) manganese (53) with Trimethylene Oxide

Trimethylamine oxide was obtained by sublimation of the dihydrate.(76) In the dry-box, 0.3 g (0.97 mmol) of acyl 53 was dissolved in 1.0 ml d_6-benzene in a round bottom flask with a stir bar. Slowly, 0.21 g (2.2 equiv) Me_3NO was added. This resulted in a great evolution of gas (CO_2) and a color change from yellow to orange. A ^{13}C NMR spectrum of the crude reaction showed only organic products 57, 58, and 59 were formed. The volatiles were vacuum-transfered and analyzed. The relative ratios of organic products are listed in Table 1. The nonvolatiles contained $Mn_2(CO)_{10}$ and an unidentified and very insoluble orange solid.

Thermal or Photochemical Reaction of Alpha-methoxycyclobutylcarbonyl(pentacarbonyl)manganese (53) with Triphenylphosphine

An equimolar mixture of acyl 53 (.35 g, 1.14 mmol) and triphenylphosphine (.61 g), dissolved in .7 ml of d_6-benzene, were added to an NMR tube with a boiling chip. The solution was heated at 55^{o} C, and monitored by ^{13}C NMR. Acyl 53 was observed to both decompose to organic products 57, 58, and 59 and also undergo phosphine substitution to yield cis- and trans-triphenylphosphinetetracarbonylmanganese(alpha-methoxycyclobutylcarbonyl) 106. Phosphine substitution occurred in roughly a 50% yield, based on NMR. These same two processes were found to occur when 53 was photolyzed at room temperature. The ratios of organic products can be found in Table 1. The synthesis of 106 is described below.

Synthesis of Alpha-methoxycyclobutylcarbonyl(triphenylphosphine)(tetracarbonyl)manganese (106)

A solution of 0.7 g 53 (2.3 mmol), 0.93 g triphenylphosphine (1.5 equiv.) and 30 ml benzene were heated at 45^{o}C under nitrogen for 2 days. The reaction was cooled to room temperature and 1.0 g of MeI (2 equiv based on phosphine) was added to precipitate any excess phosphine. The crude reaction was filtered and chromatographed on neutral alumina. The bright yellow phosphine substituted acyl band was eluted with 15/85 ethyl acetate/hexane. A minor, yellow band elutes just before the acyl band and was identified as the trans, bis-triphenylphosphine hexacarbonyldimanganese. Removal of solvents resulted in a yellow solid which was a mixture of the cis (major) and trans isomers. Analytical samples were obtained by recrystalization in hexane. Orange-yellow, opaque crystals were collected in a 15% overall yield. CHN analysis for $C_{28}H_{24}O_6PMn$, Calculated: C, 62.00; H, 4.46. Found: C, 61.72; H, 4.41. MP = 88-91° C. ^1H NMR (d_6-benzene, 300 MHz): 7.72-6.96 ppm (m, $-PPh_3$); 3.29 (s, cis -OMe); 3.20 (s, trans -OMe); 1.4-2.6 (m, ring H's). ^{13}C NMR (d_6-benzene, 75 MHz) cis isomer: 272.05 ppm / J_{PC}=14.1 Hz (acyl CO); 218.32, 216.54 / J_{PC}=21.0 Hz, 214.96 / J_{PC}=9.6 Hz (M-CO); 92.64 (alpha-ring C); 50.36 (MeO); 27.55 (beta-ring carbons) 11.74 (gamma-ring C). trans isomer: 263.40 /coupling not resolved (acyl CO); 224.94 (M-CO); 93.77 (alpha-ring C); 51.93 (MeO); 28.17 (beta-ring C); 11.91 (gamma-ring C). IR (CH_2Cl_2): 2064.5 cm^{-1} (m); 1990.8 (s); 1975.3 (s); 1956.2 (s); 1618.0 (m).

Thermolysis of Alpha-methoxycyclobutylcarbonyl(triphenylphosphine)(tetracarbonyl)manganese (106)

The thermolysis of 106 was carried out as described for 53, only at 73° C. In comparison to 53, decarbonylation of 106 was much slower and was allowed to proceed for 48 hrs before the volatiles were removed. The same three organic compounds were observed to have formed, but the relative ratios were not determined, because of the high reaction temperature employed.

Synthesis of Alpha-methoxycyclobutylcarbonyl(triethylphosphine)(tetracarbonyl)manganese (107)

In an NMR tube, a solution of 0.7 g 53 (2.3 mmol), 0.19 g PEt_3 (2.3 mmol), and 1.0 ml d_6-benzene were heated at 45° C. The reaction was closely monitored for completion of the reaction; both the formation of 107 and the complete decomposition of 53. This was necessary since 53 and 107 were found to co-chromatograph. The mono-substituted acyl complex 107 was purified by chromatography on silica gel (quartz column, indicator) with 10/90 ethyl acetate/ hexane as elutant. The rotovapping of solvents left a very viscous, pale yellow oil in a 23% yield. CHN analysis for $C_{16}H_{24}O_6PMn$, Calculated: C, 48.25; H, 6.07. Found: C, 48.38; H, 6.16. MS(CI): 399 (M + 1). ^1H NMR (d_6-benzene, 300 MHz): 3.20 ppm (s, 3 H, -OMe); 2.04-2.34 (dm, 4 H, beta-ring H's); 1.46-1.61 (m, 8 H, gamma-ring H's and -$PC\underline{H}_2$) ; 0.61-0.77 (m, 9 H, -$PCH_2C\underline{H}_3$). ^{13}C NMR (d_6-benzene, 75 MHz): 271.84 ppm / J_{PC}=12.3 Hz (acyl CO); 216 (m, M-CO); 93.10 (alpha-ring C); 50.61 (-OMe); 27.52 (beta-ring C's); 11.82 (gamma-ring C). IR (CCl_4): 2054.7 cm^{-1} (m); 1978.9 (s); 1960.9 (s); 1944.0 (s); 1583 (m).

Synthesis of Alpha-methoxycyclobutylcarbonyl(bistriethylphosphine)(tricarbonyl)manganese (109)

One gram of 53 (3.25 mmol) and 2.1 g of PEt_3 (6.5 mmol), dissolved in 25 ml benzene, were heated at 45° C for 48 hrs. Excess phosphine was removed with MeI as described above. Column chromatography with neutral alumina was performed and 10/90 ethyl acetate/hexane eluted the desired acyl complex. The yellow band was rotovapped to yield 0.7 g (54%) of a gummy solid containing some monophosphine-substituted acyl. Recrystallization from hexane at -40° C allowed for collection of .3 g (23%) of clear yellow crystals of the disubstituted acyl. CHN analysis for $C_{21}H_{39}O_5P_2Mn$, Calculated: C, 51.64; H, 8.05. Found: C, 51.58 H, 8.05. MP: 71-72° C. MS (CI): 489 (M+1); 461 (M+1 - CO). ^1H NMR (d_6-benzene, 300 MHz) 3.23 ppm (s, MeO); 1.7 (m, $PC\underline{H}_2CH_3$); 0.97 (m, $PCH_2C\underline{H}_3$); .92 - 2.13 (m, ring H's). ^{13}C NMR (d_6-benzene, 75 MHz) 285.07, 284.82, 284.57 ppm (acyl CO); 222.3, 222.1, 221.9 (M-CO); 91.92 (alpha-ring C); 48.99 (MeO); 27.31 (beta-ring C's); 20.91, 20.61 ($P\underline{C}H_2CH_3$); 12.49 (gamma-ring C); 7.72 ($PCH_2\underline{C}H_3$). IR (CCl_4) 2061.3 cm^{-1} (w); 2002.6 (m); 1977.8, 1971.9 (w); 1919.0, 1889.6 (vs).

Attempted Decarbonylation of Alpha-methoxycyclobutyl carbonyl(bistriethylphosphine)(tricarbonyl)manganese (109)

A benzene solution of the title compound was photolysed for 72 hrs at 30° C in an NMR tube. No decarbonylation was observed, and ^{13}C analysis showed the bisphosphine acyl to be photochemically unreactive. No degradation to the organic compounds 57, 58, or 59 had occurred. A benzene solution of this compound was heated to 70° C in an attempt to thermally induce decarbonylation. Even after 48 hrs, no reaction was observed. The organic degradation products 57, 58, or 59 were not formed.

Synthesis of Alpha-ethoxycyclopropane Carboxylic Acid

A solution of 2.0 g alpha-ethoxycyclopropyl bromide(39) (5.4 mmol) in 20 ml diethyl ether was cooled to -78° C under nitrogen. Gradually, 10.7 ml 1.7N t-butyl lithium (in hexane, 1.5 equiv) was added by syringe. The solution was allowed to stir for 20 min, then CO_2 was bubbled through for 10 min. After warming to room temp, the solution was acidified with 30 % HCl and extracted with diethyl ether. Rotovapping the dried extracts ($MgSO_4$) yielded 1.15 g of the viscous acid (72%). The acid was Kugelrohr-distilled from 84-92° C at .1 mm for a 48 % yield. ^1H NMR (d_6-benzene): 10.2 ppm (s, 1H, -COOH); 3.7 (q, 2H, $-OCH_2$); 1.65-1.05 (m, 7H, ring H's and Me). ^{13}C NMR (d_6-benzene); 180.5 ppm ($-CO_2H$); 65.7 (alpha-ring C); 65.3 ($-OCH_2$); 17.2 (beta-ring C's); 15.5 (Me).

The acid chloride was synthesized by stirring excess oxallyl chloride and the title compound under nitrogen for 10-15 hrs. The excess oxallyl chloride was rotovapped at room temperature at 5 mm. The acid chloride was purified by Kugelrohr-distillation; 62-80° C / 10 mm, in a 52 % yield. ^1H NMR ($CDCl_3$): 3.7 ppm (q, 2H, $-OCH_2$); 1.7-0.8 (m, 7H, ring H's and Me). ^{13}C NMR (d_6-benzene): 175.7 ppm (-COCl); 67.2 (alpha-C); 65.7 ($-OCH_2-$); 18.8 (beta-C's); 15.1 (Me).

Synthesis of Alpha-ethoxycyclopropylcarbonyl (pentacarbonyl)manganese (110)

A solution of 2.7 g of alpha-ethoxy-cyclopropyl carboxylic acid chloride (16.2 mmol) in 20 ml THF was added via cannula to a slurry of 3.8 g $KMn(CO)_5$ (16.2 mmol) in 50 ml THF. The reaction was stirred at room temperature for 24 hrs. The solvents were removed on line and the crude orange residue was extracted several times with a 1:3 mixture of CH_2Cl_2:hexane, then filtered over celite. The solvents were rotovapped to yield an orange-yellow oily residue. Chromatography on silica gel with a florescent indicator (quartz column) and 10/90 ethyl acetate/hexane resulted in elution of an almost colorless band. After removal of solvents, 1.6 g of a pale yellow oil remained (32%). Recrystallization from hexane at -40° C, several times, resulted in off-white crystals in a 20 % yield. CHN analysis for $C_{11}H_9O_7Mn$, Calculated: C, 42.87; H, 2.93. Found: C, 42.30; H, 2.85. MP= 36° C. MS (CI): 309 (M+1), 281 (M+1 - CO). ^1H NMR (d_6-benzene, 300 MHz): 0.72-1.13 ppm (m, ring H's and CH_3); 3.18 (q, $-OCH_2-$). ^{13}C NMR (d_6-benzene, 75 MHz): 257.24 ppm (acyl CO); 210.2 (br, M-CO); 80.24 (alpha-ring C); 65.14 ($-OCH_2-$); 15.14 ($-CH_3$); 14.75 (beta-ring C's). IR (CCl_4): 2114.1 cm^{-1}, 2049.7 (m); 2026.7, 20087.3 (vs); 1629.2.

Attemted Thermal or Photochemical Decarbonylation of Alpha-ethoxycyclopropylcarbonyl(pentacarbonyl)manganese (110)

Acyl 110 was found to be inert to decarbonylation when subjected to thermolysis using temperatures from 50 to 70° C and various solvents. The deuterated solvents used were benzene, acetone, acetonitrile, and THF. A slight decomposition was detected based on a broadening of the peaks in the ^1H NMR spectrum, over a time period of days. The only decomposition product detected was $Mn_2(CO)_{10}$. Similar results were obtained when 110 was subjected to photolysis with either a pyrex or quartz filter, with the aforementioned solvents.

Chemical Decarbonylation of Alpha-ethoxycyclopropylcarbonyl (pentacarbonyl)manganese (110) with Trimethylamine Oxide

In the dry box, 0.6 g of 110 (1.95 mmol) was dissolved in 1 ml CD_3CN and cooled to -40° C. Small portions of 0.32 g Me_3NO (2.2 equiv) were added gradually, as the ensuing reaction was quite vigorous. The product, 2-substituted ethoxy allyl, was chromatographed on silica gel and was eluted with 15/85 ethyl acetate/hexane. It was found to be a bright yellow oil, isolated in a 12 % yield. MS(EI): 252 (M^+). ^1H NMR (d_6-benzene, 300 MHz): 4.65 ppm (d, 1H, =C$\underline{H}$-OEt); 4.25-4.34 (m, 1H, 2-allylic); 3.07-3.33 (m, 2H, OCH_2); 1.73 (dd, 1H, syn 3-allylic); 0.87 (t, 3H, Me); 0.57 (dd, 1H, anti 3-allylic). ^{13}C NMR (d_6-benzene, 75 MHz): 110.0 ppm (2-allylic); 76.3 (=$\underline{C}$H-OEt); 68.4 (OCH_2); 25.5 (3-allylic); 14.5 (Me). IR (CCl_4): 2048 cm^{-1} (w), 1965 (s), 1942 (s).

Synthesis of Alpha-deuteriocyclopropane Carboxylic Acid

Alpha-deuteriocyclopropyl cyanide$^{(77)}$ was prepared by a literature method and hydrolysed with aqueous HCl. Instead of a distillation of the crude carboxyllic acid, which was reported to give a low yield of 18%, another procedure was followed. The acidic solution was extracted 3 times with a saturated $NaHCO_3$ solution, then back extracted with ether (to remove unhydrolysed organic cyanide). This was followed by acidification (35% HCl), extraction with ether (3X, 50 mls) and drying the extracts with $MgSO_4$. Rotovapping the ether at 10 mm resulted in a clear viscous oil in a 62% yield. ^{13}C NMR ($CDCl_3$): 181.3 ppm (CO_2H); 12.5 (J_{CD}=102 Hz, CD); 8.9 (CH_2).

The acid chloride was made using oxallyl chloride, as described previously. Kugelrohr-distillation from 52-72° C at 60 mm gave a 56% yield of the pure acid chloride.

Synthesis of Alpha-deuteriocyclopropylcarbonyl (pentacarbony)manganese (131)

The title compound was made by the method of Stone(41) using alpha-deuteriocyclopropane carboxylic acid chloride. Sublimation at 45° C/.1 mm onto a dry ice/acetone probe provided off-white crystals in 46% yield. ^2H NMR (benzene, d_6-benzene as reference): 2.17 ppm (-CD). ^1H NMR (d_6-benzene): 2.2 ppm (-CH, 95% deuterated); 0.8-1.4 (m, $-CH_2$). ^{13}C NMR (d_6-benzene): 252.0 ppm (acyl CO); 210.3 (M-CO); 40.4 (J_{CD}=35.3 Hz, -CD); 11.1 ($-CH_2$).

Reaction of Triphenylphosphine with Alpha-deuteriocyclopropylcarbonyl(pentacarbonyl)manganese

Equivalent amounts of 131 and triphenylphosphine were refluxed in degassed cyclohexane for 12 hrs, as previously described by Stone et al.(41) The solvents were removed on line to yield a bright yellow oil, later identified as the allyl complex 133. A deuterium NMR of the crude reaction mixture showed that one resonance was present at 3.95 ppm. This indicated that the deuterium label was at the 2-position (or central position) as shown by structure 133. 2H NMR (benzene, 300 MHz): 3.95 ppm (-CD). ^{13}C NMR (d_6-benzene, 75 MHz): 227.1 ppm /J_{PC}=60 Hz (M-CO); 93.6 (unresolved m, -CD); 44.9 (-CH_2).

Synthesis of 7-Chloro,7-thiophenylbicyclo(4.1.0)heptane (142)

A solution of 5.1 g trichloroisocyanuric acid (21.9 mmol) in 50 ml CCl_4 was cooled to 0° C, while stirring under nitrogen. Slowly, a pre-cooled solution of 8.5 g 5-thiophenylbicyclo(4.1.0) heptane(81) was added and the reaction was stirred for 12 hrs. After filtering the reaction mixture through a medium glass frit, and removal of solvents at reduced pressure, the title compound was purified by column chromatography. A 50/50 mixture of hexane/methylene chloride eluted 142 on silica gel. The product was obtained as a mixture of isomers in a yield of 77%.

Synthesis of 7-Methoxy,7-thiophenylbicyclo(4.1.0)heptane (143)

A slurry of 4.2 g 142, (17.6 mmol), 3.9 g $CdCO_3$ (22 mmol), and 100 mls MeOH were cooled to 0° C under nitrogen.

Solid $AgBF_4$, (4.1 g, 21 mmol) was added and the reaction stirred for 6 hrs while warming to room temperature. The crude reaction was filtered over celite and the MeOH rotovapped at 40° C at 20 mm. The title compound was purified by column chromatography, 50/50 hexane/ethyl acetate on silica gel (quartz column with indicator). Compound 143 was isolated in a 65% yield as a mixture of both the endo and the exo isomers.

Synthesis of 7-Methoxybicyclo(4.1.0)heptyl 7-Carboxylic acid (144)

A dark green solution of the napthyl radical anion was obtained by stirring a solution of 0.27 g Li, cut into small pieces (38.4 mmol), 4.9 g napthalene (38.4 mmol), and 150 ml dry THF for 16 hrs. The reaction was then cooled to -78° C and 3.0 g of 143 (12.8 mmol) was added via cannula. The solution was allowed to warm slowly, while watching for a color change from green to red; this occurred around -5° C. (At times, this color change did not occur, but 144 was still synthesized by the same method.) The reaction was stirred at this temperature for 10 min, then cooled again to -78° C. Cylinder CO_2 was bubbled in for 15 min, accompanied by another color change to orange. After warming to room temperature, water was SLOWLY added, followed by saturated sodium bicarbonate. The crude reaction was extracted 3 times with diethyl ether, 50 ml, then acidified with 35% HCl. Extraction with diethyl ether, drying of the extracts with $MgSO_4$, and rotovapping at room temperature under reduced pressure resulted in a 57% yield of solid acid, 144. Only the exo isomer was obtained.

The corresponding acid chloride, 145 was synthesized using neat oxallyl chloride and worked up as previously described. Kugelrohr-distillation from 110° C to 135° C at 20 mm gave the acid chloride in a 45% yield.

Synthesis of Endo 7-Methoxybicyclo(4.1.0)heptyl,7-carbonyl (dicarbonyl)(η^5-cyclopentadienyl)iron (146)

A solution of 1.3 g of acid chloride 145 (6.9 mmol) in 15 ml THF was added via cannula to a slurry of 1.55 g KFp (6.9 mmol) in 40 ml THF. The reaction was stirred for 12 hrs and purified by column chromatography on alumina. A solvent mixture of 95/5 hexane/ethyl acetate resulted in elution of the desired acyl complex as a bright yellow band. The compound was recrystallized from hexane to yield 0.8 g (77%) of needle-like yellow crystals. X-Ray quality crystals were precipitated slowly from dilute hexane solutions (Figure 6). CHN Analysis for $C_{16}H_{18}O_4Fe$, Calculated: C, 58.21; H, 5.49. Found: C, 58.10; H, 5.52. MP= 120° C. MS(EI): 330 (M+). ^{1}H NMR (d_6-benzene, 300 MHz): 4.31 ppm (s, 4.3 H, Cp); 3.09 (s, 2.9 H, $-OCH_3$); 1.83 (m, 4 H, $-CH_2$); 1.43 (m, 2 H, -CH); 1.25 (m, 4 H, $-CH_2$). ^{13}C NMR (d_6-benzene, 75 MHz): 256.08 ppm (acyl CO); 216.03 (M-CO); 87.02 (Cp); 82.18 (-C-OMe); 55.64 ($-OCH_3$); 25.31 (-CH); 21.64, 19.09 ($-CH_2$). IR (CCl_4): 2019 cm^{-1}, 1966, 1635.

Photolysis of 7-Methoxybicyclo(4.1.0)heptyl,7-carbonyl (dicarbonyl)(n^5-cyclopentadienyl)iron (146)

A solution of 0.3 g 146 (0.91 mmol) in 0.8 ml d_6-benzene was photolyzed at room temperature and monitored by ^{13}C NMR. Rearrangement of the title compound occurred slowly and it was necessary to photolyze for 3 days for ca. 75% conversion. The contents of the NMR tube were poured on top of a silica gel column packed with hexane. Increasing percentages (v/v) of diethyl acetate in hexane were used to develop the column. A mixture of 10/90 ethyl acetate/hexane eluted unreacted acyl complex 146. A mixture of 15/85 ethyl acetate/hexane eluted 2 red bands, the first was Fp_2 and the second was the minor carbene complex 148. Removal of the solvents from the carbene complex 148 band resulted in light red crystals in a 10% yield. CHN Analysis for $C_{15}H_{18}O_3Fe$, Calculated: C, 59.63; H, 6.00. Found: C, 59.70; H, 6.04. MP= 162° C. ^1H NMR (d_6-benzene, 300 MHz): 4.36 ppm (s, Cp); 3.80 (s, $-OCH_3$); 2.44 (m, $-\underline{C}H-C-OMe$); 2.24 (m, $-\underline{C}H-C=O$), 1.44 to 1.00 (m, $-CH_2$). ^{13}C NMR (d_6-benzene, 75 MHz): 347.5 ppm (=C-OMe), 266.6 (acyl CO); 217.45 (M-CO); 87.16 (Cp); 66.00, 64.00, 61.67 ($-OCH_3$ and 2 -CH-), 28.00, 24.24, 23.50, 23.14 ($-CH_2$). IR (CCl_4): 1997 cm^{-1}, 1949, 1647.

The remaining red band, left near the top of the column, was eluted with 40/60 ethyl acetate/hexane and yielded 34% of a red oil after removal of the solvents. The oily carbene complex 147 could be recrystallized from hexane solutions at -30° C to give dark red crystals. CHN

Analysis for $C_{15}H_{18}O_3Fe$, Calculated: C, 59.63; H, 6.00. Found; C, 59.50; H, 6.01. MP= 76 to 77° C. MS(EI): 302 (M^+, 100%). ^1H NMR (d_6-benzene, 300 MHz): 4.27 ppm (s, Cp); 3.81 (s, $-OCH_3$); 2.6 (m, -CH-C-OMe); 2.35 (m, -CH-C=O); 1.48 to 1.21 (m, $-CH_2$). ^{13}C NMR (d_6-benzene, 75 MHz): 351.90 ppm (=C-OMe); 267.88 (acyl CO); 217.78 (M-CO); 85.76 (Cp); 67.77, 66.28, ($-OCH_3$ and -CH-C=O); 61.83 (-CH-COMe); 27.04, 24.52, 24.29, 23.30 ($-CH_2$). IR (CCl_4): 2006 cm^{-1}, 1951, 1674, 1652.

Reaction of Anti 1-(Carbonyl-η^5-cyclopentadienyl),2-methoxyferracyclopent-2-ene-5-one,3,4-tetramethylene (147) with d_3-MeONa in d_4-MeOH

A solution of 147 (0.15 g, 0.15 mmol) and 0.7 ml d_4-methanol was cooled to -60° C and both a ^1H and a ^{13}C NMR spectrum were recorded. Approximately 0.1 ml of a 2% (by mass) solution of Na in d_4-methanol was added, after cooling the NMR tube to ca. -200° C with liquid N_2. Spectra were taken immediately, after warming the tube to -60° C. The only reaction that had occurred was deuterium exchange on the carbon alpha to the carbenic carbon. This was evident because a new triplet at 63.5 ppm had replaced the singlet at 63.5 in the ^{13}C spectrum and the ^1H resonance at 2.25 ppm had completely collapsed. The tube was warmed to 24° C by increments of 10° C and either a ^1H or ^{13}C spectra taken. At -20° C new peaks were observed in the ^{13}C spectrum. These could not be assigned to a structure because of the non-detection of any new complexes by chromatography techniques. The NMR tube was then heated to 40° C under a N_2 atmosphere and spectrally monitored. After 4 hours, complex 147 was observed to rearrange to the minor carbene complex 148. The ratio of 148 reached a maximum after 24 hrs, and did not appreciably change for 72 hrs. Only by TLC was it possible to ascertain that 147 had also rearranged to the acyl complex 146.

Thermolysis of Anti 1-(Carbonyl-n^5-cyclopentadienyl)-2-methoxyferracyclopent-2-ene-5-one,3,4-tetramethylene (147) in d_4-Methanol

A solution of 0.1 g of 147 in 0.7 ml d_4-methanol was heated at 40° C in an oil bath and maintained under N_2. Periodic monitoring by ^{13}C NMR failed to show any conversion to the minor carbene isomer 148. Reaction times were continued for up to 7 days. Complex 147 was decomposing to undetermined products. The thermolysis in CD_3OD did result in deuterium exchange at the alpha carbon as was described above in the reaction of sodium methoxide with complex 147, in d_4-methanol.

Reaction of Anti 1-(Carbonyl-n^5-cyclopentadienyl)-2-methoxyferracyclopent-2-ene-5-one,3,4-tetramethylene (147) with d_4-Acetic Acid in d_6-Acetone

A solution of 0.15 g 147 (.05 mmol) in 0.7 ml d_6-acetone was cooled to -60° C and ^1H and ^{13}C spectra recorded. The sample was then cooled to -200° C and 0.05 ml d_4-acetic acid was added and mixed into solution. Spectra recorded from -60° C to 40° C showed that complex 147 was completely stable to these conditions, as no new resonances were detected. Furthermore, this sample was heated at 45° C for three days and no 148 was detected. Complex 147 proved to be quite stable under these conditions, as only 2 new and extremely small "Cp" resonances were observed in the ^{13}C spectrum.

Photolysis of Anti 1-(Carbonyl-n^5-cyclopentadienyl)-2-methoxyferracyclopent-2-ene-5-one,3,4-tetramethylene (147) in d_6-Benzene

A solution of 0.15 g 147 and 0.7 ml d_6-benzene were photolyzed at 30° C and monitored by nmr. After 30 hrs, it was evident that rearrangement to the minor carbene complex 148 had occurred. Approximately 66% of 147 and 33% of the syn complex 148 were present.

Synthesis of 7-Methoxybicyclo(4.1.0)heptyl,7-carbonyl (pentacarbonyl)manganese (155)

A solution of 1.3 g 145 (6.9 mmol) in 20 ml THF was added to a slurry of 1.65 g $KMn(CO)_5$ (6.9 mmol) in 40 ml THF, via cannula, at 25° C. The reaction was stirred under N_2 for 24 hours. The solvents were removed on line. The orange-yellow residue extracted with 10/90 ethyl ether/hexane and filtered through Celite. After rotovapping, the oily residue was chromatographed on silica gel. The desired acyl complex 155 was eluted with a 10/90 ethyl acetate/hexane solution and was clearly visible as a bright yellow band. The title complex was obtained as a bright yellow oil in a 40% yield. CHN Analysis for

$C_{14}H_{13}O_7Mn$, Calculated: C, 48.29; H, 3.76. Found: C, 48.44; H, 3.80. MS(EI): 348 (M^+). ^1H NMR (d_6-benzene, 300 MHz): 3.01 ppm (s, $-OCH_3$); 1.75, 1.66 (m, -CH-); 1.4 to 1.1 (m, $-CH_2-$). ^{13}C NMR (d_6-benzene, 75 MHz): 259.8 ppm (acyl CO); 210.4 (M-CO); 83.0 (-$\underline{C}$OMe); 56.1 ($-OCH_3$); 26.8 (-CH-); 21.3, 18.6 2($-CH_2$). IR (CCl_4): 2110.3 cm^{-1}, 2022, 2007, 1628.

Thermolysis of 7-Methoxybicyclo(4.1.0)heptyl,7-carbonyl (pentacarbonyl)manganese (155)

A solution of 0.35 g 155 (1 mmol) in 0.8 ml d_6-benzene was heated in an oil bath at 65° C under a N_2 atmosphere. Decarbonylation was observed to be slow and steady. The rearrangement was monitored by ^{13}C NMR which showed that two new acyl carbene complexes (75% major and 20% minor) and an unidentified complex 158 (5%) were the only new products. After 48 hours, the contents of the tube were chromatographed on silica gel. A mixture of 15/85 ethyl acetate/hexane eluted these three new products as a single orange-yellow band. Various solvent mixtures were used in TLC experiments for further separation of these compounds, but without success. The unknown complex 158 could be separated by heating a mixture of these compounds at 65° C for 4 days. The carbene complexes 156 and 157 were unstable under these conditions and decomposed to unidentified "vinyllic" compounds. Complex 158 could be chromatographed using the previous conditions and was found to be a bright yellow viscous oil. ^1H NMR (d_6-benzene, 300 MHz): 3.2 ppm (s, $-OCH_3$); 0.7 to 2.3 (m, ?). ^{13}C NMR, APT (d_6-benzene, 300 Hz): 328.1 (?) ppm ; 205.3; 89.1 (odd); 58.0 (odd); 47.4 (odd); 28.0 (odd); 22.3 (even); 22.0 (even); 20.3 (even). A selective recrystallization of the major carbene could be achieved by cooling an ethyl acetate/hexane solution to -30° C. Bright yellow crystals precipitated from solution. These were not of good quality for x-ray, but this continues. MS (HR): 320.0107 (theoretical: 320.0092). ^1H NMR (d_6-benzene, 300 MHz): 3.88 ppm (s, $-OCH_3$); 2.3 (m, -CH-); 1.8 to 0.6 (m, $-CH_2$). ^{13}C NMR (d_6-benzene, 75 MHz): 357.5 ppm (=C-OMe); 266.0 (acyl CO); 217 to 212 (M-CO); 75.9, 69.7, 68.7 ($-OCH_3$, -CH-); 28.5, 27.5, 25.4, 25.3 ($-CH_2$). IR (CCl_4): 2066 cm^{-1}, 2011, 1972, 1950, 1660. "Minor Acyl Carbene" ^1H NMR (d_6-benzene, 300 MHz): 3.84 ppm (s, $-OCH_3$). ^{13}C NMR (d_6-benzene, 300 MHz): 362.1 ppm (=C-OMe), 268.7 (acyl CO); 217 to 212 (M-CO); 68.4, 63.9. (Other resonances cannot be assigned with certainty).

Synthesis of 2-Methylcyclopropyl Carboxylic Acid Chloride

The corresponding acid was purchased from Aldrich and was found to be a mixture of trans and cis isomers in a respective ratio of 85% to 15%. The acid was treated with excess oxallyl chloride and worked up as previously described. Kugelrohr-distillation from 45 to 55° C at 40 mm yielded pure acid chloride.

Synthesis of 2-Methylcyclopropylcarbonyl(pentacarbonyl) manganese (210)

To a slurry of 2.4 g KMn(CO)$_5$ (10 mmol) in 30 ml THF was slowly added, via cannula, 1.2 g 2-methylcyclopropyl carboxylic acid chloride (10 mmol) dissolved in 20 ml THF. The reaction was stirred for 36 hrs and then the solvents were removed on line. The yellow solid which remained was sublimed from 60^o C to 100^o C at < 0.1 mm. The sublimate was roughly a 3 to 1 mixture of the title compound to Mn$_2$(CO)$_{10}$. The acyl complex was further purified by chromatography on silica gel with 90/10 ethyl acetate/hexane as elutant. The purified acyl was found to form white needle-like crystals and was rather insoluble in a variety of common solvents. CHN analysis for C$_{10}$H$_7$O$_6$Mn, Calculated: C, 43.18; H, 2.52. Found: C, 43.15; H, 2.51. MP: 72^o C (dec). MS (CI): 279 (M+1); 251 (M+1 - CO). ^{1}H NMR (d$_6$-benzene, 300 MHz): 2.1 ppm (m, -CHCOMn); 0.76 (d, J$_{HH}$=5.6 Hz, Me); 1.4-0.2 (m, -CH$_2$ and -C$\underline{H}$Me). ^{13}C NMR (d$_6$-benzene, 75 MHz): 250.1 ppm (acyl CO); 210.4 (M-CO); 50.45 (-CH-COMn); 20.46, 17.64, 10.74. IR (CCl$_4$): 2114.2 cm^{-1}, 2050, 2011, 1632.

Thermolysis of 2-Methylcyclopropylcarbonyl(pentacarbonyl) manganese (210)

The 2-methyl cyclopropyl manganese acyl complex 210, 0.34 g (0.11 mmol) and 1.0 ml d$_6$-benzene were heated at 65^o C. Decarbonylation was observed to occur very slowly; the reaction required 7 days for completion under these conditions. A single product, the syn crotyl pi-allyl complex 211, was detected. ^{13}C NMR (d_6-benzene, 75 MHz): 94.0 ppm (-CH-); 62.8 (-CHMe); 36.5 ($-CH_2$); 19.9 ($-CH_3$).

Photolysis of 2-Methylcyclopropylcarbonyl(pentacarbonyl) manganese (210)

Attempts to decarbonylate 210 were unsuccessful when a Pyrex filter was used. However, the use of a quartz filter did result in decarbonylation, albeit slow. The photolysis was carried out at 15° C to avoid possible isomerization of any anti crotyl pi-allyl that might be formed. A control, composed of a known mixture of syn and anti pi-allyls, was also photolyzed for the duration of the experiment. When the solvent used was d_6-benzene or d_3-acetonitrile the solubility of 210 was rather limited at 15° C, and it was necessary for long reaction times, ie days. The only product detected was the syn crotyl pi-allyl complex 211. The ratio of syn to anti allyls in the control mixture remained constant. Anti crotyl pi-allyl complex 212: ^{13}C NMR (d_6-benzene, 75 MHz): 90.7 ppm (-CH-); 61.7 (-CH-Me); 42.5 ($-CH_2$); 18.0 ($-CH_3$).

Synthesis of Syn and Anti Crotyl Pi-Allyl Complexes of Tetracarbonyl Manganese

An 85% to 15% mixture of trans and cis sigma crotyl pentacarbonyl manganese complexes(78) were photolysed at 25° C using a quartz filter in d_6-benzene. The stereochemistry about the double bond was most likely retained since a ratio of 85 to 15, syn to anti crotyl pi-allyl complexes was obtained. It was necessary to photolyze to completion since the pi-allyls and the sigma complexes co-chromatographed on alumina or silica gel with hexane as eluant. ^{13}C NMR (d_6-benzene): syn isomer, 222 ppm (br, M-CO); 94.0 (-CH-); 62.8 (-CHMe); 36.3 ($-CH_2$); 19.9 (Me). anti isomer, 222 ppm (M-CO); 90.7 (-CH-); 61.7 (-CHMe); 42.5 ($-CH_2$); 18.0 (Me).

Thermal Conversion of Anti Crotyl Pi-Allyl Complex (212) to Syn Crotyl Pi-Allyl Complex (211)

An 85/15 mixture of syn/anti crotyl pi-allyls of tetracarbonyl manganese were subjected to the same conditions as in the thermolysis of **210** i.e., 65° C. Within 24 hrs, all of the anti isomer **212** had isomerized to the syn isomer **211** as determined by ^{13}C NMR spectroscopy.

Synthesis of 1-Methylcyclopropyl Carboxylic Acid Chloride

Excess oxallyl chloride was reacted with 1-methylcyclopropyl carboxylic acid (Aldrich) and worked up as previously described. Purification was achieved by Kugelrohr-distillation from 55° C to 90° C at 50 mm.

Synthesis of 1-Methylcyclopropylcarbonyl(dicarbonyl)(n^5-cyclopentadienyl)iron (184)

To a slurry of 1.8 g KFp in 40 ml THF, cooled to 0° C, was added 1.0 g of alpha-methylcyclopropyl acid chloride in 20 ml THF via cannula. The reaction was stirred for 12 hrs and prepared for column chromatography as previously described. On silica gel, a 10/90 diethyl ether/hexane solvent mixture eluted the desired acyl band, which closely followed Fp_2. After rotovapping the solvents, shiny opaque yellow crystals of the acyl were obtained in a 75% yield. CHN analysis for $C_{12}H_{12}O_3Fe$; Calculated: C, 55.42; H, 4.65. Found: C, 55.34; H, 4.69. MP=59-60° C. MS(CI): 261 (51%, M+1); 204 (100%, M+1 -2CO). ^1H NMR (d_6-benzene, 300 MHz): 4.15 ppm (s, Cp); 1.28 (s, Me); 1.24, 0.33 (m, $-CH_2-$). ^{13}C NMR (d_6-benzene, 75 MHz): 252.6 ppm (acyl CO); 215.5 (M-CO); 86.0 (Cp); 42.1 (-CMe); 22.7 ($-CH_3$); 16.6 ($-CH_2-$). IR (CCl_4): 2021 cm^{-1}, 1961, 1654, 1624.

Photolysis of 1-Methylcyclopropylcarbonyl(dicarbonyl)(n^5-cyclopentadienyl)iron (184)

Complex 184, 0.3 g (0.12 mmol) in 0.7 ml d_6-benzene, was photolysed for 48 hrs using a pyrex filter. Initially, only the sigma complex 185 was detected by ^{13}C NMR spectroscopy (from 1 to 20 hrs). Only after 24 hrs was the n^3-methallyl pi-complex 186 detected in this mixture. Both isomers, exo and endo, were present at 24 hrs in roughly equal amounts, but after 48 hrs the ratio of exo to endo had increased to roughly 3 to 1, respectively. The sigma complex 185 can be isolated from the photolysis mixture by chromatography on neutral alumina. It is the first of the two yellow bands eluted with hexane (the second is the pi-allyl complex 186). Alkyl Complex 185; MS (CI): 233 (1%, M+1); 205 (7%, M+1 - CO); 177 (11%, M+1 -

2CO); 57 (100%, Fe). ^{13}C NMR (d_6-benzene, 25 MHz): 217.6 ppm (M-CO); 86.2 (Cp); 38.9 ($-CH_2$); 19.1 ($-CH_3$).

Synthesis of n^3-Methallyl(carbonyl)(n^5-cyclopentadienyl) iron (186)

For purposes of comparison and confirmation of the identity of the pi-allylic compound formed in the photolysis of 184, complex 186 was synthesized by the method of Rosenblum.(64) ^{13}C NMR (d_6-benzene): exo isomer, 91.2 ppm (-CMe); 79.7 (Cp); 34.8 ($-CH_2$); 27.1 ($-CH_3$).

Synthesis of 2,3-Trans Diethylcyclopropylcarbonyl (dicarbonyl)(n^5-cyclopentadienyl)iron (213)

The same procedure as for synthesis of 184 was followed using equivalent amounts of KFp and the acid chloride of 2,3-trans diethylcyclopropyl carboxyllic acid (70-90° C / 20 mm). Elution of this bright yellow acyl band with hexane on neutral alumina resulted in a 41% yield of a red-yellow oil, after removal of solvents. CHN Analysis for $C_{15}H_{18}O_3Fe$, Calculated: C, 59.65; H, 5.96. Found: C, 59.35; H, 6.17. MS(CI): 303 (100%, M + 1). ^1H NMR (d_6-benzene, 300 MHz): 4.28 ppm (s, $-OCH_3$); 2.4 (q, -CH-COFp); 1.7 to 1.0 ($-CH_2$-, -CH-Et); 0.92 (t, $-CH_3$); 0.82 (t, $-CH_3$). ^{13}C NMR (d_6-benzene, 75 MHz): 248.4 ppm (acyl CO); 215.6, 215.3 (M-CO); 86.38 (Cp); 53.81 (-CH-COFp); 35.88, 31.81 (-CH-Et); 26.90, 20.62 ($-CH_2$-); 14.59, 13.46 ($-CH_3$). IR (CCl_4): 2359 cm^{-1}, 2339, 2017, 1960, 1644.

Photolysis of 2,3-Trans Diethylcyclopropylcarbonyl(dicarbonyl)(η^5-cyclopentadienyl)iron (213)

A solution of 0.3 g of 213 (0.1 mmol) and 0.7 ml d_6-benzene was photolyzed at room temperature with a pyrex filter. The major reaction reaction was decarbonylation resulting in alkyl migration to form the alkyl complex 214. After 3 hrs, a new Cp resonance appeared at 79.8 ppm. This is characteristic of exo pi-allyl complexes. The relative amount of this "allylic" complex 215 did not increase, even after continued photolysis for 3 days. Photolysis with a quartz filter gave similar results. Alkyl Complex 214; MS(CI): 275 (22% M + 1); 247 (47.8 %, M + 1 - CO). ^{1}H NMR (d_6-benzene, 300 MHz): 4.2 ppm (s, Cp); 1.6 to 0.1 (m). ^{13}C NMR (d_6-benzene, 75 MHz): 217.89, 217.62 (M-CO); 30.97 (-CH_2-); 30.62 (-CH-Et); 27.93 (-CH_2-); 15.12, 14.29 (-CH_3); 7.41 (-CH-Fp). IR (CCl_4): 2008 cm^{-1}, 1952.

Synthesis of 2-Methylcyclopropylcarbonyl(dicarbonyl)(η^5-cyclopentadienyl)iron (193) and (202)

A solution of 2.0 g 2-methylcyclopropyl acid chloride (Aldrich) (16.9 mmol) in 20 ml THF was added to a slurry of 3.6 g KFp (16.9 mmol), which was cooled to 0° C. After stirring for 15 hrs, 100 ml hexane was added to the crude reaction, which was then filtered over celite and rotovapped. Chromatography on neutral alumina with 100% hexane resulted in the separation of a yellow band. After removal of solvents, the acyl was obtained as a red-yellow oil in 35% yield. The acyl was found to have a melting point of 21° C. Analysis showed the acyl to be an 86/14 mixture of trans/cis isomers. CHN analysis for $C_{12}H_{12}O_3Fe$; Calculated: C, 55.42; H, 4.65. Found: C, 55.49; H, 4.70. MS (CI): 261 (M + 1). ^1H NMR (d_6-benzene, 300 MHz): 4.9 ppm (s, Cp); 3.05 (m, cis -CH-COFp); 2.75 (m, trans -CH-COFp); 0.9-2.0 (m, Me and other ring H's). ^{13}C NMR (d_6-benzene): 249.6 ppm (acyl CO); 215.27, 215.12 (M-CO); 86.3 (Cp); 49.0 (trans -CH-COFp); 46.1 (cis -CH-COFp); 19.43, 19.32, 18.0 (trans -CH-Me, $-CH_2$, $-CH_3$); 18.5, 15.6, 12.7 (cis -CH-Me, $-CH_2$, $-CH_3$). IR (CCl_4) 2021.6 cm^{-1} (s); 1960.6 (s); 1640.7 (m).

Photolysis of Cis and Trans 2-Methylcyclopropylcarbonyl (dicarbonyl)(η^5-cyclopentadienyl)iron (193) and (202) Mixture

A solution of 0.3 g of the title mixture (0.11 mmol) and 0.7 ml d_6-benzene were photolyzed at 15° C in an NMR tube. The reaction was periodically monitored by NMR and was found to decarbonylate rather slowly. Decarbonylation and alkyl migration to form alkyl complexes 196 and 197 were relatively rapid, in comparison to the ring-opening reaction to form pi-allyl complexes. The photolysis was continued for 40 hrs at which time the following complexes were evident; 196, 197, 194, 195, Fp_2 and ferrocene.

Synthesis of Trans/Cis Mixture of Fp Crotyl Sigma Complexes

The title compounds were made according to a literature method.(79) The corresponding syn and anti crotyl allyls were also made according to reference 79. The ^1H NMR spectra of the mixture of syn/anti allyls corresponded to the published spectra. The ^{13}C assignments for the syn and anti allyls could therefore be made as follows. [Exo,syn 194]: ^{13}C NMR (d_6-benzene, 75 MHz): 222.6 ppm, (M-CO); 79.4 (Cp), 75.4 (-CH-); 53.0 (-CH-Me); 29.5 (-CH_2); 21.8 (-CH_3). [Exo,anti 198]: ^{13}C NMR (d_6-benzene, 75 MHz): 222.6 ppm (M-CO); 79.4 (Cp); 72.4 (-CH-); 50.3 (-CH-Me); 33.8 (-CH_2-); 18.4 (-CH_3). [Endo,syn 195]: ^{13}C NMR (d_6-benzene, 75 MHz); 82.5 ppm (Cp); 92.8 (-CH-); 55.1 (-CH-Me); 32.5 (-CH_2-); 22.4 (-CH_3).

Stability Study of a Mixture of Syn and Anti Crotyl Pi-Allyl Complexes of FeCOCp Using ^{13}C NMR Integration

A mixture of the title compounds (198 and 194) was photolyzed in d_6-benzene for 8 hrs at 15° C. At this time, a constant amount of the endo,syn complex 195 was obtained. Any change in the amount of exo,anti 198 relative to exo,syn 194 could thus be determined. A pulse delay of 15 s was used for obtaining spectra based on T1 studies. A pulse width of 8.7 us and an acquisition time of 1.64 s were used in conjunction with this pulse delay. The decoupler was on only during the acquisition time to reduce any NOE effects. The results of integration of the 8, 24, 48 and 72 hour reaction spectra are shown in Table 2 as ratios of exo,syn to exo,anti isomeric carbons. The ratios remain consistent, and show that the exo,anti isomer is stable to these conditions.

Synthesis of Trans and Cis 2-Methylcyclopropyl(dicarbonyl)(n^5-cyclopentadienyl)iron (196) and (197)

A solution of 1.2 g (6.9 mmol) of cis and trans 2-methylcyclopropyl bromide(80) and 25 ml THF were added by cannula to a slurry of 1.5 g KFp (6.9 mmol). The reaction was stirred at room temperature for 18 hrs. The crude reaction was filtered over celite and rotovapped to leave a dark red, gummy residue. Column chromatography on neutral alumina with hexane as the eluant resulted in collection of a bright yellow band. Rotovapping the solvents left a reddish-yellow oil, isolated in 8.1% yield. The oil was composed of both the cis and trans 2-methylcyclopropyl Fp sigmas in a relative ratio of 30 to 70, respectively. The major product in this reaction was FpBr. MS (CI): 232 (21.3%, M + 1); 205 (62.7%, M + 1 - CO). ^{1}H NMR (d_6-benzene, 300 MHz): 4.17 ppm (s, cis Cp); 4.12 (s, trans Cp); 1.20 (d, trans $-CH_3$); 1.16 (d, cis $-CH_3$); 1.40 to -0.16 (m, ring H's of both isomers). ^{13}C NMR (d_6-benzene, 75 MHz): 217.3 ppm (cis and trans M-CO); 85.4 (cis and trans Cp); 22.1, 17.4, 17.2, -0.2 (trans isomer); 19.4, 15.4, 11.8, 0.4 (cis isomer). IR (CCl_4): 2011 cm^{-1}, 1955.

Photolysis of Trans / Cis Mixture of 2-Methylcyclopropyl (dicarbonyl)(η^5-cyclopentadienyl)iron (196) and (197)

A solution of 0.32 g of the 70/30 196/197 mixture and 0.8 ml d_6-benzene was photolyzed with a pyrex filter at room temperature. After 24 hours of photolysis both exo,syn, endo,syn and exo,anti isomers are detected by ^{13}C NMR. After 48 hrs the relative amount of syn isomer (exo and endo) to anti isomer (exo) was 86 to 14. An identical solution was photolyzed in the presence of ruthenocene, as an internal standard. The appearance of exo,syn and endo,syn isomers correlated well with the dissappearance of the trans alkyl complex 196.

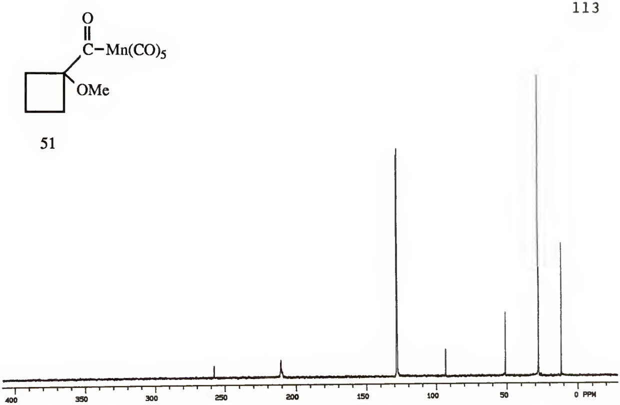


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Figure 11. ^{13}C NMR spectrum of complex 51.

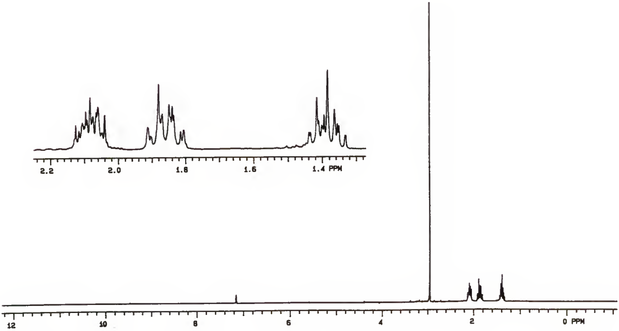
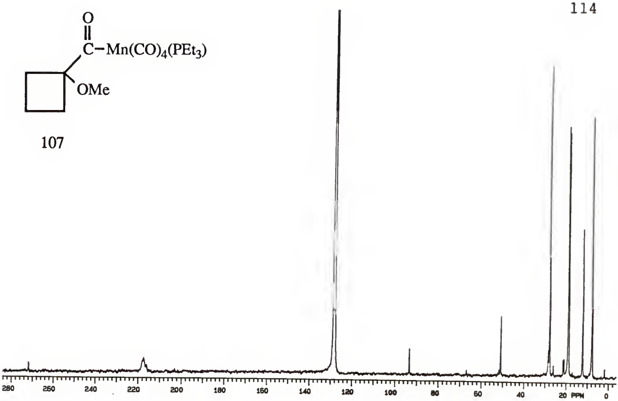


Figure 12. ^{1}H NMR spectrum of complex 51.



107

Figure 13. ^{13}C NMR spectrum of complex 107.

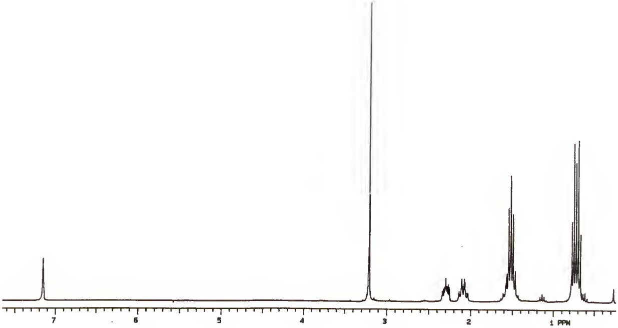


Figure 14. ^{1}H NMR spectrum of complex 107.

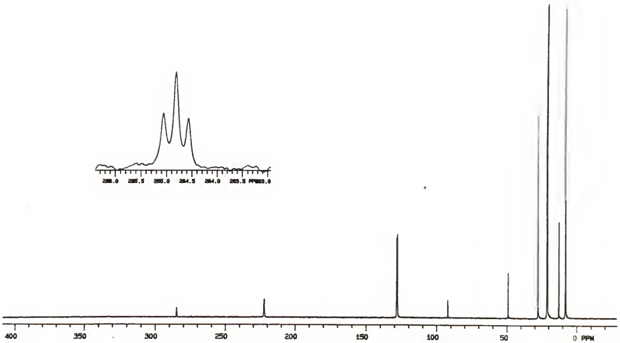


Figure 15. ^{13}C NMR spectrum of complex 109.

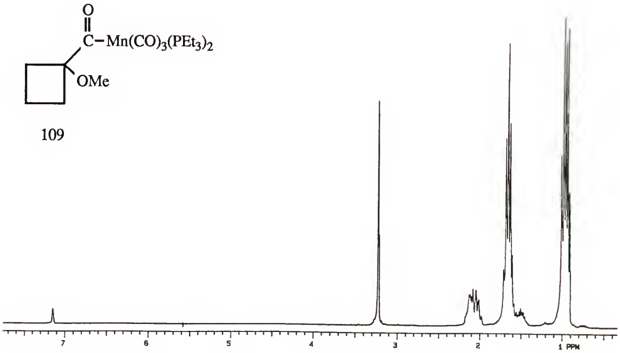
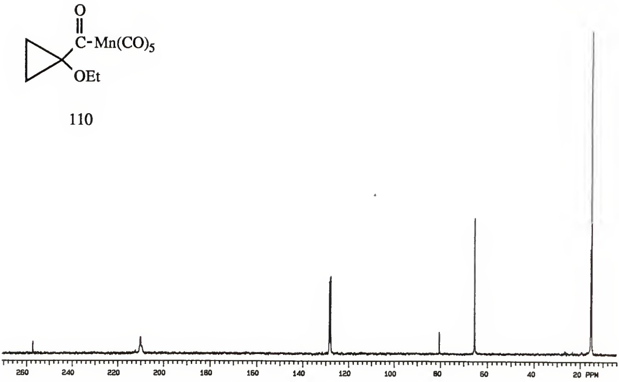


Figure 16. ^{1}H NMR spectrum of complex 109.



110

Figure 17. ^{13}C NMR spectrum of complex 110.

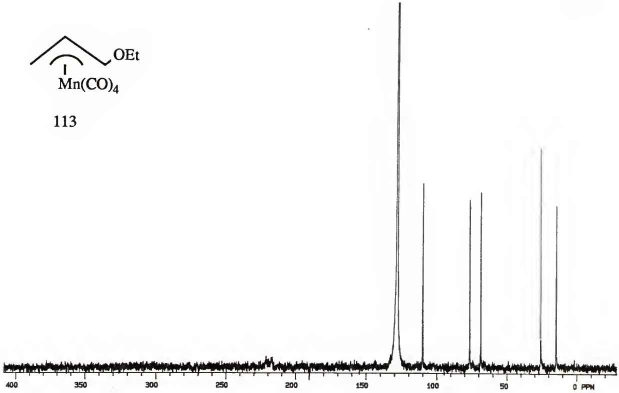


Figure 18. ^{13}C NMR spectrum of complex 113.

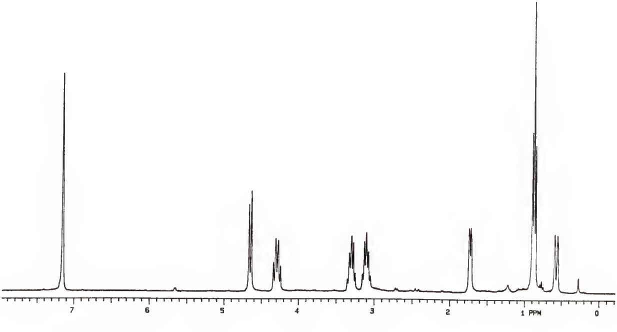


Figure 19. ^{1}H NMR spectrum of complex 113.

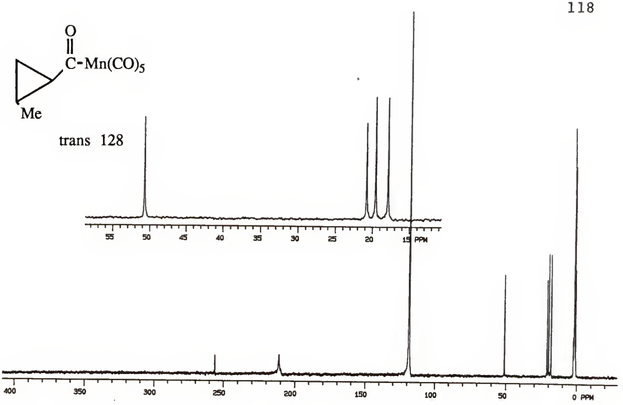


Figure 20. ^{13}C NMR spectrum of complex 128 in CD_3CN.

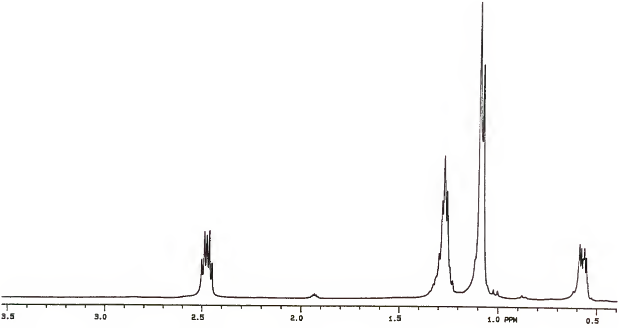
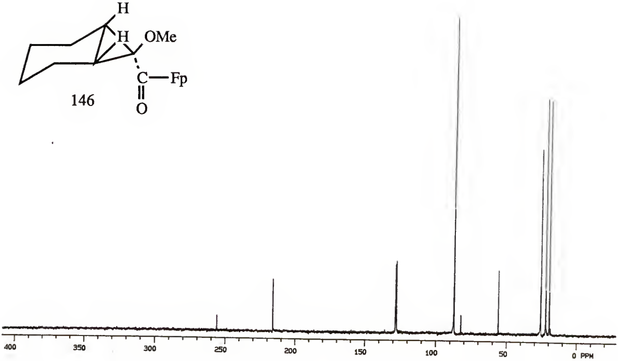


Figure 21. ^{1}H NMR spectrum of complex 128 in CD_3CN.



146

Figure 22. ^{13}C NMR spectrum of complex 146.

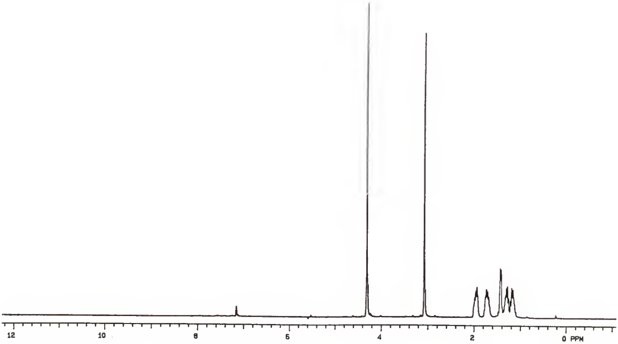


Figure 23. ^{1}H NMR spectrum of complex 146.

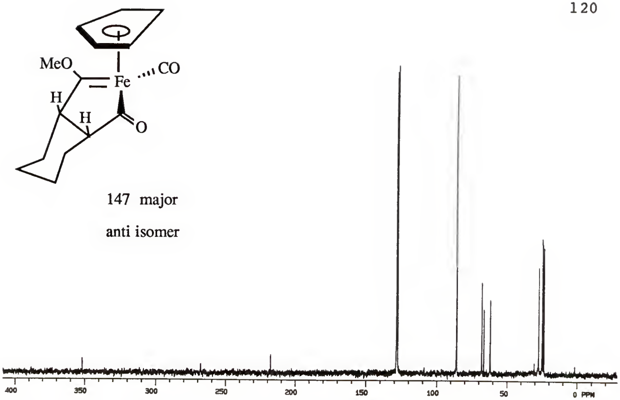


Figure 24. ^{13}C NMR spectrum of complex 147.

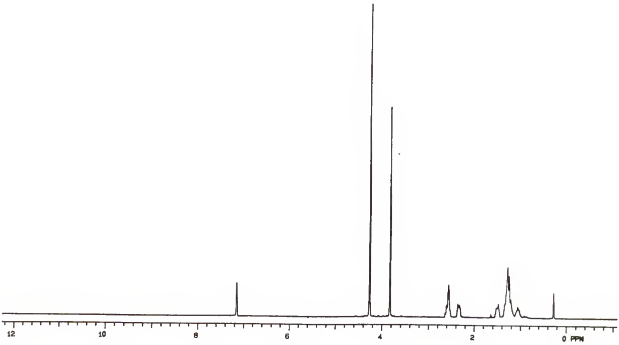


Figure 25. ^{1}H NMR spectrum of complex 147.

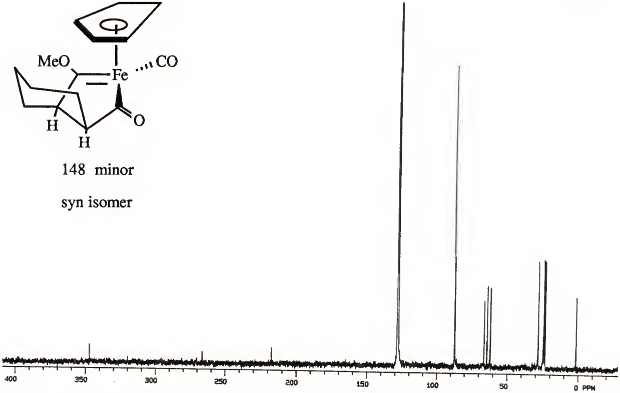


Figure 26. ^{13}C NMR spectrum of complex 148.

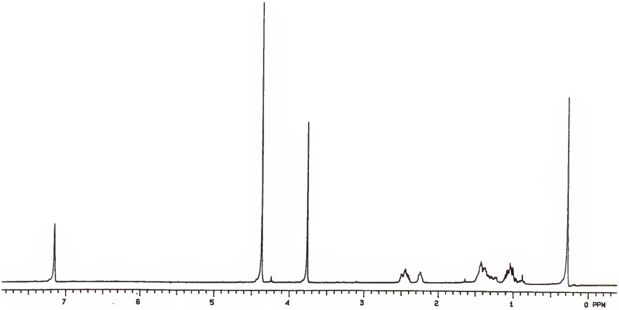


Figure 27. ^{1}H NMR spectrum of complex 148.

155

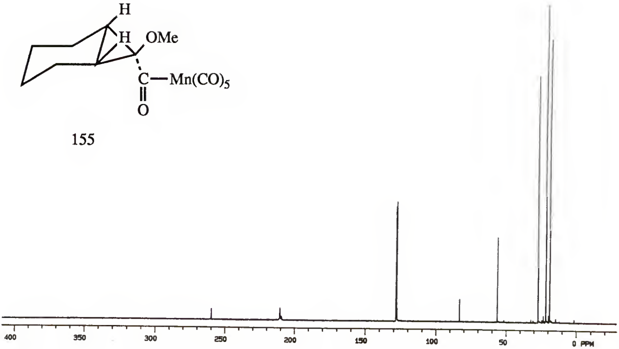


Figure 28. ^{13}C NMR spectrum of complex 155.

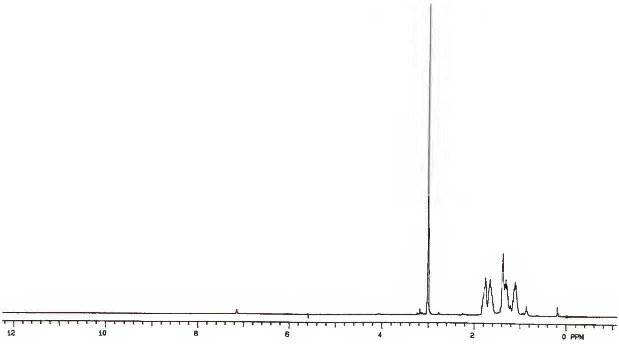


Figure 29. ^{1}H NMR spectrum of complex 155.

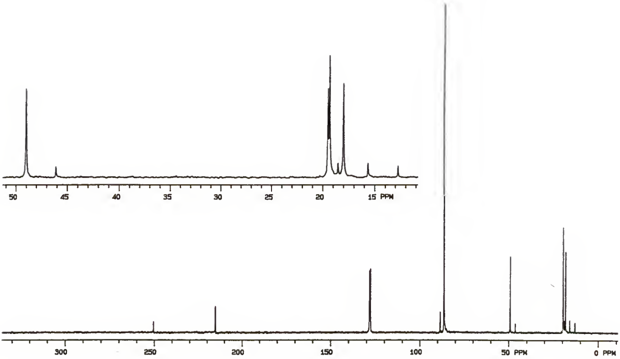


Figure 30. ^{13}C NMR spectrum of complexes 193 and 202.

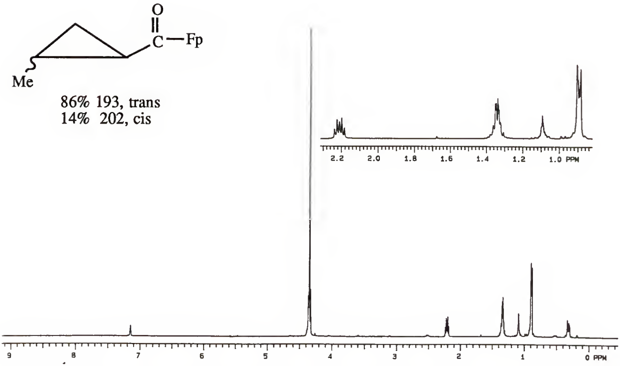


Figure 31. ^{1}H NMR spectrum of complexes 193 and 202.

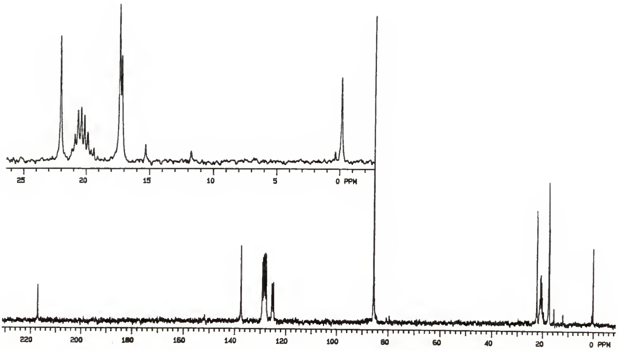


Figure 32. ^{13}C NMR spectrum of complexes 196 and 197 in d_8-toluene.

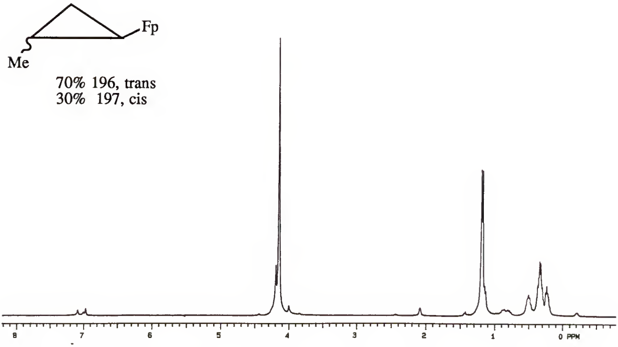
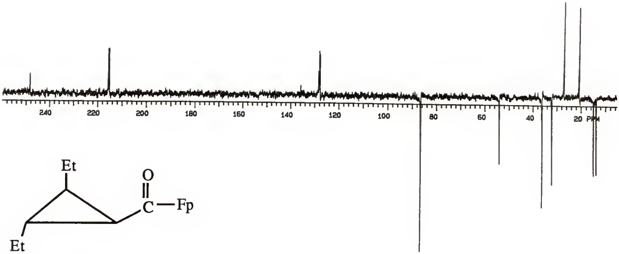


Figure 33. ^{1}H NMR spectrum of complexes 196 and 197 in d_8-toluene.



213

Figure 34. ^{13}C NMR (APT) spectrum of complex 213.

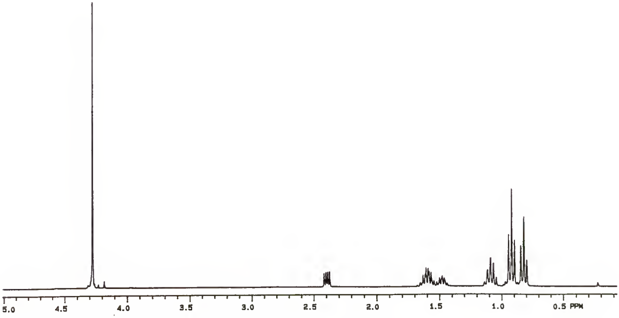
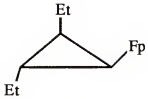


Figure 35. ^{1}H NMR spectrum of complex 213.



214

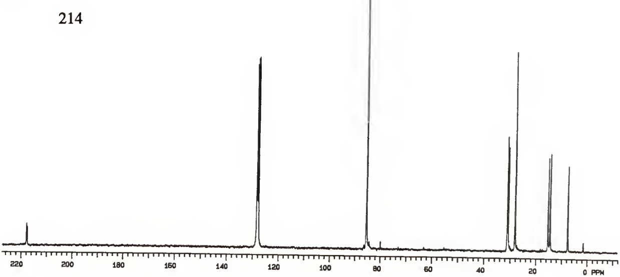


Figure 36. ^{13}C NMR spectrum of complex 214.

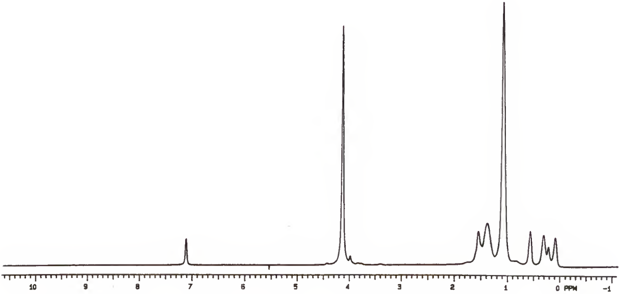


Figure 37. ^{1}H NMR spectrum of complex 214.

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BIOGRAPHICAL SKETCH

The author was born on August 27, 1957, in Spartanburg, South Carolina. She spent her formative years in Jacksonville, Florida and went from the first through the twelfth grades in that city. After going to many undergraduate institutions, she graduated with a BS in Chemistry from Jacksonville University in 1982. In 1983 she began graduate work at the University of Florida, where she worked with Dr. William M. Jones.

The author has many cats and dogs, and one husband. Hobbies include quilting, training dogs ang jogging.

The author has accepted a post-doctoral position with Richard Jordan at the University of Iowa.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William M. Jones, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Merle A Battiste
Merle A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William R Dolbier
William R. Dolbier, Jr.
Professor of Chemistry

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John G. Dorsey
Associate Professor of
Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John R. Sabin
Professor of Physics

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 1989

Dean, Graduate School